New improved polymer electrolyte membrane for PEM fuel cell. Final report 1: Documentation Synthesis and Test of Proton Exchange Membranes

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Final Report, 1

Documentation Synthesis and Test of Proton Exchange Membranes

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Discussion, Summary and Conclusion

The overall aim of this project has been to synthesize, characterise and test proton exchange membranes (PEM) for fuel cell (FC) operation in order to achieve better durability of the PEM. The overall project targets were as follows:

Membrane: Conductivity >0.2 S/cm @ 25ºC
Stability: >5,000 hours
Cost: <60 US$ per m^2

MEAs: Voltage @ 1 A/cm^2: 0.7 V up to 130ºC

Available PEMs are almost exclusively of the perfluorinated type, which offer good proton conductivity and reasonable durability in FC applications. However, these PEMs are only available at high cost. Consequently there is a huge incentive to synthesize/develop PEM that may be produced at substantially lower cost. The present project has been looking at developing alternatives to the perfluorinated PEMs and has been partly based on results obtained in PSO project no. 4073, 'PEM brændselscelle med ny polymer elektrolyt membran', where promising results were obtained.
The project was inaugurated in April 2006 and ended in March 2009.

The three (3) active project partners and their responsibilities are listed below:

- IRD Fuel Cells A/S [IRD], responsible for the following:
  - Project coordination
  - PEM synthesis and pilot synthesis by grafting techniques
  - FC durability testing of PEM
- Department of Chemical- Bio- and Environmental Technology [SDU] being main responsible for the following
  - PEM characterisation
  - FC durability testing of PEM
- Department of Chemical- and Biochemical Engineering [DTU] being main responsible for the following:
  - PEM synthesis from constituent monomers
  - PEM characterisation

A novel concept for preparation of sulfonate containing fluorinated block copolystyrenes have been developed based on initial ATRP of fluorinated styrene monomers. The strategy depends on well defined macrointiators that after conversion to block copolymers can be post functionalized in two steps with propylsulfonate groups in different ratios. Thermal investigations have demonstrated that addition of a PFS block to the sulfonate containing block improves the materials' thermal stability.
The novel block copolymer materials' potential as polymer electrolytes for fuel cells is yet to be investigated. This will be attempted after conversion of the sulfonate salts to sulfonic acids. In a future development and in order to simplify the experimental work not least the post derivatizations attempts will be made to prepare sulfonate containing fluorinated monomers. If successful the preparation will be followed by polymerization experiments with subsequent polymer electrolyte membrane evaluations. In a different approach surface initiated ATRP of sulfonate containing monomers onto PVDF-membranes shall be attempted.

By irradiating different fluoropolymer films, ETFE and PVdF, with electrons the polymers have been grafted. Instead of using styrene as monomer, which is more prone to radical attack, the monomers have been isomeric mixture of meta-/para-methylstyrene and para-tert-butylstyrene, α-

methyl styrene and methacrylonitrile. Divinylbenzene has been used as cross linker to obtain better electrochemical stability.
The grafting conditions and apparatus have been optimised with savings of up to 50% – 75% being realised. However, the substitution of the harsh chlorosulfonic acid with milder sulfonating agents, like has not been achieved.

α-methyl styrene does not produce consistent grafting results and the grafted polymer is not temperature stable at normal FC operating conditions. The dynamic monomer volume does have an effect on the grafting yield, hence para-tert-butylstyrene does not graft as well as meta-/para-methylstyrene. Different sulfonating techniques have been investigated with chlorosulfonic acid being the most effective. Generally grafted polymers with conductivities as good or better than Nafion® are achieved, however they are brittle and if not stabilised with a cross linker they exhibit poor stability in chemical tests, which examines their stability towards radical attack. Grafted membranes have lower methanol permeability than Nafion® and are also good candidates for DMFC membranes.

The best synthesized membranes with respect to conductivity were prepared by radiation grafting with methyl styrene. The choice of monomer did influence the conductivity and although the monomer was chosen both for minimising the cost, improving the stability towards radical attack as well as yielding a good conductivity it produced fragile membranes. Conductivity values up to ~0.15 S/cm were obtained. This is roughly twice the value of the current industry standard (Nafion®), however, it is not as high as the project target of 0.2 S/cm @25°C. Substantial effort was devoted to improve the grafting in the surface of the film, however, this was not realised and it is believed to be one of the reasons for not obtaining the target value. Another reason for not obtaining the targeted conductivity is related to the fragility in the dry state. The fragility limits the degree of grating that can be used – high degree of grafting is easily obtained, however, at the cost of fragile membranes. The fragility is partly believed to be related to conformational stress within the membrane. There are indications that the fragility may be alleviated by dissolving and recasting the grafted, sulfonated polymer thus allowing for the proton conducting moieties to orient themselves towards one another (like in Nafion®) and improving the conductivity this way. Unfortunately a thorough investigation of this reorienting effect was not conducted.

The brittleness of the membranes did not allow for fuel cell testing of the membranes and durability has only been tested outside FC's. Thus, in Fenton's test, the use of different substituted styrene monomers improve the oxidative/radical stability compared to pure styrene grafted membranes. Compared to Nafion®, however, the membranes are not as durable in the Fenton's test and clearly deteriorate faster. Correlation of test results from Fenton's test with fuel cell data has not revealed unambiguous results, thus Fenton's test cannot be used alone as a selection guide.

Several commercial perfluorinated membranes have been tested in a stack with a reformat gas. They show similar stability compared to Nafion®, however, thick membranes are more stable than thinner membranes.
The poor film forming properties of membranes synthesised from constituent monomers and the fragility of the radiation grafted membranes resulted in membranes that could not be fabricated into a Membrane Electrode Assembly, MEA. The membrane tended to crack during the MEA fabrication process and unfortunately the brittleness of the grafted polymer prohibited FC testing. Consequently fuel cell testing was not conducted. Testing of commercial membranes at temperatures up to 130°C were not done (only op to ~80°C) since it is well known that they start to loose their conductivity above this temperature.

The results with directly synthesised membranes indicate that conducting membranes should be attainable by switching to less rigid monomers. Likewise there are also indications that carefully synthesised polymers of opposite charge may yield conducting membranes. For the grafted membranes reduction of the brittleness seems to be important to remedy and will be addressed in a

project to come by looking at the possibility of dissolving and recasting the membrane. Also the possibility to incorporate the sulfonate group and/or other proton conducting groups via the irradiation/grafting method in the polymerisation step will be investigated. The method for incorporating metal oxides into a membrane has reached a level where reproducible results are attained. Metal oxides are believed to stabilise the proton conducting membrane in several ways and physical characterisation and FC testing of these benign effects need to be demonstrated.

The present project has contributed with essential knowledge on synthesis of conducting polymers from constituent monomers and development of radiation grafted PEM. The method for grafting polymer films via radiation methods has been scaled to be able to handle pilot scale fabrication of PEM and it is estimated that the requirement of ~30 €/m^2 can be met. This is approximately half the forecasted price of ~60 €/m^2 indeed a substantial reduction.

The project results has been published in 2 peer reviewed papers and 2 masters thesis's as well as several presentations at symposiums and conferences.

The development of membranes for FC will be continued by the same consortium as well as doctor Patric Jannasch at Lunds University in the project 'New macromolecular architectures and functions for proton conducting fuel cell membranes' funded by the Danish Council for Strategic Research through contract no. 09-065198.

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1 Introduction.

This final report deals with the synthesis and test of polymers for Proton Exchange Membranes (PEM).
The synthesis of PEM's has been carried out at The Danish Polymer Centre (DPC) at The Technical University of Denmark and at IRD Fuel Cells A/S (IRD) and has been conducted both by the staff at IRD and students from University of Southern Denmark (SDU).
The report is divided into 4 sections:

1. Development of PEM conducted at DPC, see chapter 2.
2. Development of PEM conducted at IRD, see chapter 3.
3. Physical characterisation of PEM conducted at SDU and IRD, see chapter 4.
4. Testing of PEM, see chapter 5.

1.1 Objectives.

The purpose of this project is to develop a Polymer Electrolyte Membrane (PEM, also referred to as Proton Exchange Membrane) to be used in a fuel cell as the separator between the positive and negative electrode.

The objectives of the project were the development of:

1. Synthesis of a Polymer Electrolyte Membrane (PEM) with the following characteristics:
   - Conductivity > 0.3 S/cm.
   - Stability > 5000 hours.
   - Cost < 30 US$/$m^2$.

   To prepare a Membrane Electrode Assembly (MEA) with optimised structures such that:
   - Power density 0.7 W/cm^2 @ 1.0 A/cm^2 (70°C, ambient pressure)
2. Physical and chemical characterisation of the PEM with respect to stability.

While fuel cell tests of promising new electrolytes will be conducted especially conductivity is a good indicator for new electrolyte candidates.

2 Synthesis of Fuel Cell Membranes

2.1 Introduction, PEM synthesis conducted at DPC

Our original approaches for the synthesis of novel polymers for proton conducting membranes aimed at preparation of block copolymers containing sulfonate groups. However, the known strong tendency of sulfonate groups to dissolve in water[1] due to their ability to form aggregates with ionic regions exposed to the aqueous solution should be suppressed. The undesired water solubility is anticipated to be avoided if the non-ionic block is highly hydrophobic e.g. a fluoropolymer. Initially we followed two different lines.

In a first approach we've focused on the possibility of direct polymerization of sulfonic acid or sulfonate containing monomers in a controlled manner. However, the only available monomer appears to be 2-acrylamido-2-methyl-N-propanesulfonic acid (AMPS).

In the second approach we've turned our attention to entirely fluorinated backbones. Fluorinated vinyl monomers can easily be transformed to numerous, diverse functional materials by use of controlled radical polymerization techniques.[2] 2,3,4,5,6-Pentafluorostyrene (PFS) in particular has been successfully introduced to several linear di- and multiblock copolymers by atom transfer radical polymerization (ATRP)[3,4,5]. By use of a polyether based macroinitiator triblock copolymers with short outer PFS blocks were prepared[6]. These materials intended as solid Li-battery electrolytes demonstrated competitive Li^+ conductivity. Similarly, very hydrophobic fluorinated nanoparticles based on PFS were prepared either from a hexafunctional initator or a hexafunctional PS macroinitiator[5]. FS has additionally been the source for both *p*-substituted methoxy[7] (TFMS) or fluoroalkoxy[4] tetrafluorostyrene derivatives that subsequently were transformed in a controlled manner to homopolymers as well as block copolymers by ATRP. Thin films of the polymers based on the fluoroalkoxy monomers form very low energy surfaces[4]. Furthermore, PTFMS-*b*-PS block copolymers could be demethylated to the *p*-hydroxytetrafluorostyrene analogues that functioned as templates for derivatization with various hexyl-linked azobenzenes aiming at materials for optical storage[7]. In the search for alternative materials intended for polymer electrolytes for fuel cells the template strategy was adapted aiming at possible introduction of pendant sulfonates.

In a final approach the synthetic possibilities to prepare oppositely charged polymer side-chains were exploited. The water uptake of ionomer membranes can be reduced by introduction of specific interactions, e.g. dipole-dipole, electrostatic or hydrogen bonding[8]. The oppositely charged polyelectrolytes are generally known to form stable interpolymer complexes[9]. It has been already demonstrated that some acid-base blend membranes prepared by mixing polysulfonates and polybases show better thermal and mechanical stabilities compared to the sulfonated polymers alone and performed very well in fuel cells[10,11].

The results of the different strategies are reported in the folllowing section, where the main emphasis is devoted to the synthetic routes to the novel sulfonate containing fluorinated

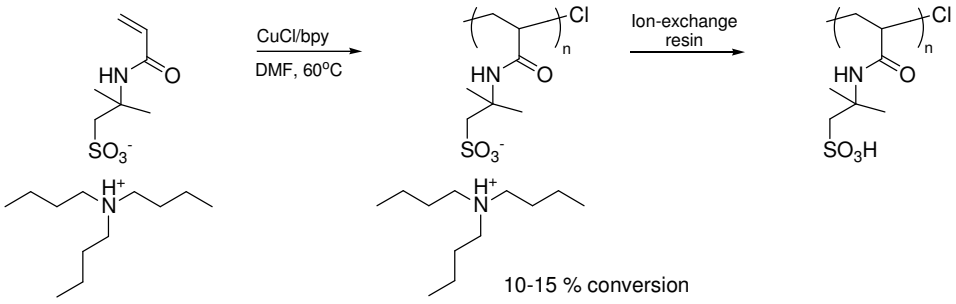
copolymers. In addition some initial evaluations of the thermal properties of these novel copolymers are presented.

2.2 Results and Discussion

2.2.1 Attempts for Controlled Polymerization of 2-acrylamido-2-methyl-*N*-propanesulfonic acid (AMPS) and Synthesis of Different Polymer Architectures Containing Ionic Segments.

2.2.1.a. Homopolymerization.

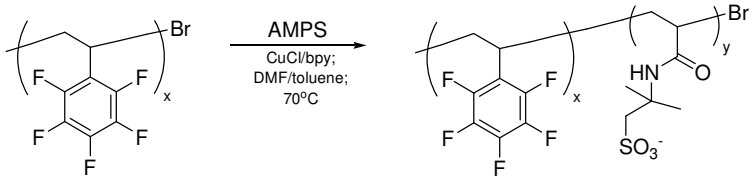
There are only few examples of controlled polymerization of acidic monomers because of the sensitivity of most living polymerizations to acidic conditions. The first successful controlled polymerization of the sodium salt of AMPS was achieved by Sumerlin et al[12]. via aqueous RAFT. The ATRP of ionic monomers is still challenging due to their interaction with the catalyst[13]. Recently, successful water-based ATRPs of AMPS-sodium salt with high degree of monomer conversion were reported[14,15]. However, we were unable do reproduce these results. The only ATRP-system for AMPS which we succeeded to reproduce was that described by Matyjaszewski *et al*[16]. The authors used *N,N*-dimethylformamide (DMF) as a solvent and 2,2'-bipyridine (bpy) as a ligand. They also used the bulky tributylammonium salt of AMPS to minimize the interaction between the catalyst and the sulfonic acid group (Scheme A). Even so, the monomer conversion was limited to 10-15 % which was also confirmed from our experiments.



Scheme A. ATRP of AMPS.

2.2.1.b. Block Copolymer Comprising Fluorinated Segment and a Short PAMPS-Block.

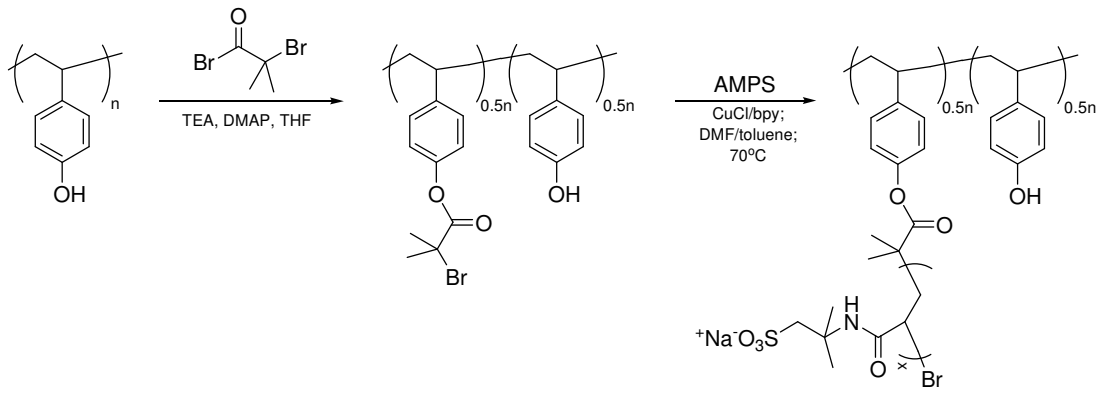
The macroinitiator approach was applied to synthesize copolymer containing highly hydrophobic fluorinated block and a short ionic sequence. PFS prepared via ATRP bearing end bromine group was used to initiate the polymerization of AMPS-sodium salt (Scheme B). Although the monomer conversion was low it was enough to attach a short ionic block to PFS. The block copolymer was soluble in tetrahydrofuran and was characterized by ^{1}H NMR and SEC analyses. The SEC trace of the block copolymer showed monomodal mass distribution (PDI 1.1) and was shifted towards higher molar masses compared to the macroinitiator.



Scheme B. Synthesis of PFS-*b*-PAMPS copolymer.

2.2.1.c. Graft copolymer with poly(hydroxystyrene) (PHS) backbone and PAMPS side chains.

The copolymer was obtained in two steps applying the 'grafting from' approach as illustrated in Scheme C. The first step was the preparation of macroinitiator containing a number of initiating sites. The commercially available PHS was reacted with 2-bromoisobutyryl bromide to convert 50 mol % of the hydroxyl groups into 2-bromo isobutyrates. In the second step these groups were used to initiate the ATRP of AMPS-sodium salt in DMF/toluene solvent mixture, bpy as a ligand and CuCl as a catalyst. Upon completion of the polymerization the product precipitated from the solution and was insoluble in most of the common solvents.



Scheme C. Synthesis of PHS-*g*-PAMPS copolymer.

2.2.2 Controlled Synthesis of Fluorinated Block Copolymers with Pendant Sulfonates[17].

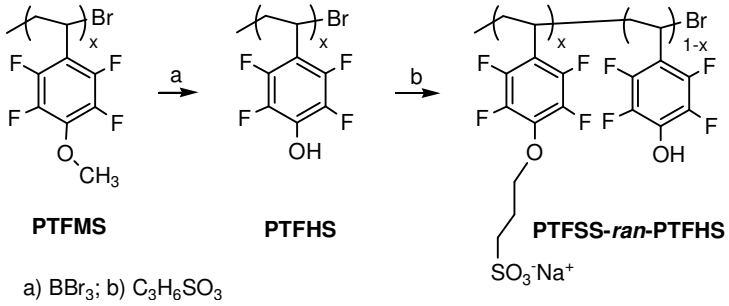
2.2.2.a. Model Reactions.

Initially the efficiency of the sulfopropylation proposed for monomers18[18] was evaluated on an activated poly(hydroxystyrene) (PHS). The *p*-hydroxyl groups of PHS were converted to phenoxides by an equimolar amount of NaOH in water followed by addition of a 10 mol% excess of 1,3-propanesultone (PrS). The phenoxides ensured nucleophilic ring-opening of PrS followed by sulfoprolylation of PHS. Subsequent dialysis removed excess of PrS and a completely water soluble product could be isolated in 95% yield. ^{1}H NMR in D_2O demonstrated close to 100% functionalization in contrast to previously reported sulfoalkylation reactions on polymer backbones that ended up with degrees of substitution between 50 and 70%[19,20,21]. Previously increased substitution levels were achieved by use of up to 9 fold molar excess of sulfoalkylation agent[22]. or application of sequential reactions[23].

2.2.2.b. Fluorinated Copolymers with Randomly Distributed Sulfonate Groups.

PTFMS (Scheme D) with different molecular characteristics were prepared by ATRP of 2,3,5,6-tetrafluoro-4-methoxystyrene (TFMS) in bulk as previously described[7]. ^{1}H NMR could be employed for exact number average molecular weight assessment by use of the defined end group from the initiator 1-phenylethyl bromide. PTFMS1 (M_n = 3400) was demethylated with BBr_3 as previously described[6] to provide a fluorinated polymer, PTFHS1 with ~ 95% hydroxyl groups. The PTFHS1 was then used as a backbone for attaching different amounts (from 100 to 14 mol%) of pendant sodium sulfonates linked through the

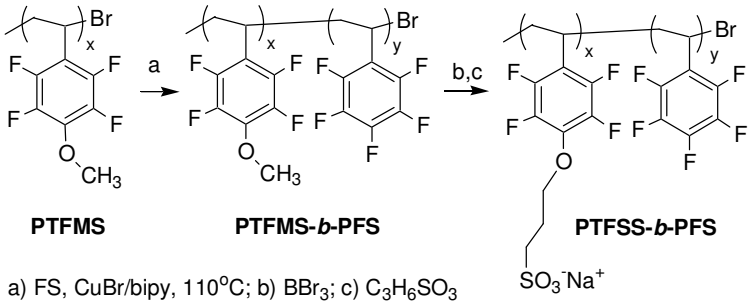
propyl spacer (Scheme D). The sulfopropylation was performed by backbone activation in a methanolic solution of NaOH. The product with nearly 100% sulfopropylation was water soluble but insoluble in DMF, DMSO and THF. The polymers with lower degrees of sulfopropylation (PTFSS-*ran*-PTFHS with 14 and 26 mol% sulfopropyl groups), on the other hand, only swelled in water, but were soluble in DMF and DMSO.



Scheme D. The principle sulfopropylation route to fluorinated polystyrenes.

2.2.2.c. Fluorinated Block Copolymers with Sulfonate Blocks.

Fluorinated block copolymers (PTFMS-*b*-PFS, Scheme E) were synthesized by ATRP of FS in bulk by use of PTFMS macroinitiators. These macroinitiators were initially prepared by ATRP of TFMS where the polymerization was stopped at between 30 and 50% TMFS conversion in order to assure a high degree of bromine end functionalization that was confirmed by ^{1}H NMR, Table 1.



Scheme E. Preparation of sulfonated fluorinated block copolymers.

Different FS content in the block copolymers was achieved by use of macroinitiators (PTFMS) with different molar mass or by varying the monomer to macroinitiator ratio. Thus block copolymers (PTFMS-*b*-PFS) with FS content from 93 to 55 mol% were obtained (Table 1). The molar ratio between TFMS and FS in the copolymers was very close to or the same as the theoretical one. SEC analyses allowed indicative molecular weights (based on PS calibrations) and the polydispersity indices (PDI) < 1.3 to be determined. Figure 1 shows the SEC traces of the macroinitiator PTFMS3 and one of the block copolymers, PTFMS3-*b*-PFS1, prepared from this macroinitiator. The macroinitiator efficiency is also demonstrated from these traces since no evidence of the macroinitiator is observed in the block copolymer trace.

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With knowledge of the molar mass and the functionality of the PTFMS macroinitiators (from ^{1}H NMR), the degree of FS polymerization was calculated from the ratio of the integral of the methoxy protons from PTFMS at 4.0 ppm to the integral of methylene and methine backbone protons at 2.9-1.8 ppm. The block copolymer molar masses calculated from ^{1}H NMR are listed in Table 2.2.2c.1.

Polymer	*Polymerization*						*Modification*		
	M_n[a] g/mol	M_n[b] g/mol	M_w/M_n[b]	PFS_{tar}[c] mol%	PFS_{exp}[c] mol%	Yield %	OH[a] mol%	SO_3[a] mol%	SO_3[d] mol%
PTFMS2	4200	5100	1.24	0	0	30			
PTFMS2-*b*-PFS1	53300	58100	1.27	94	93	82			
PTFHS2-*b*-PFS1							84		
PTFSS2-*b*-PFS1								n.s.[e]	8
PTFMS3	10300	11400	1.21	0	0	51			
PTFMS3-*b*-PFS1	21400	21800	1.25	55	55	87			
PTFHS3-*b*-PFS1							60		
PTFSS3-*b*-PFS1								60	59
PTFMS3-*b*-PFS2	24400	25900	1.28	60	60	94			
PTFHS3-*b*-PFS2							78		
PTFSS3-*b*-PFS2								n.s.[e]	78
PTFMS3-*b*-PFS3	31900	32000	1.29	70	71	92			
PTFHS3-*b*-PFS3							71		
PTFSS3-*b*-PFS3								71	69
PTFMS3-*b*-PFS4	44700	49000	1.28	80	79	93			
PTFHS3-*b*-PFS4							80		
PTFSS3-*b*-PFS4								n.s.[e]	79

Table 2.2.2.c.1 Molecular weights and compositions of fluorinated block copolystyrenes with methoxy (PTFMS-*b*-PFS), hydroxy (PTFHS-*b*-PFS), and propylsulfonate (PTFSS-*b*-PFS)) substitution.

[a] Calculated by ^{1}H NMR (in DMSO-d_6).

[b] Determined by SEC in THF (PS calibration).

[c] The target PFS content (PFS_{tar}) in the copolymers is calculated from the monomer to macro-initiator ratio.

[d] Determined by acid-base titration.

[e] non-soluble.

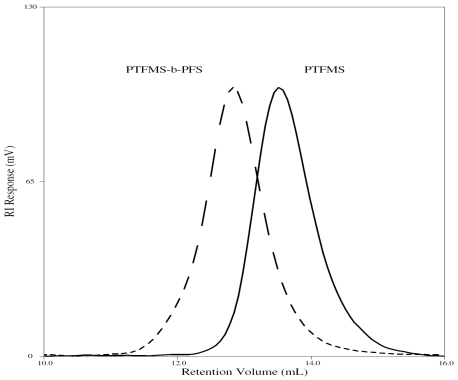


Figure 2.2.2.c.1. SEC traces of a macroinitiator (PTFMS3) and a block copolymer (PTFMS3-*b*-PFS1) in THF.

The values are generally slightly lower than M_n obtained from SEC. However, the M_ns obtained from SEC are only indicative since the calculations are based on PS standards. The methoxy containing block copolymers (PTFMS-*b*-PFS) were similarly converted to the hydroxyl containing analogues (PTFHS-*b*-PFS) through a demethylation reaction with BBr_3 in methanol (Scheme E) with degrees of functionalization in the 60-84% range (OH (mol%), Table 1) followed by sulfopropylation with PrS (SO_3 (mol%), Table 1). The resulting block copolymers (PTFSS-*b*-PFS) with sulfopropylated blocks were insoluble in common solvents when the degree of OH conversion in the hydroxyl precursor was 80% and above. When the degree of OH conversion is 70% or less, the sulfopropylated block copolymers dissolve in DMF and DMSO at 80 ^{o}C and stay in solution upon cooling. The improved solubility is most likely due to the presence of significant amounts of methoxy groups left in the sulfopropylated block. Thus, in reality one of the blocks in itself is a comonomer block with both methoxy and sulfopropyl monomers. The complete conversion of hydroxyl into sulfopropyl groups was demonstrated by ^{1}H NMR analyses in DMSO. A spectrum of the demethylated block copolymer (PTFHS3-*b*-PFS1) with 60 mol% of the methoxy groups converted to hydroxyl is shown in Figure 2.2.2.c.2 a, with the resonance corresponding to -O*H* at 11.2 ppm. After sulfopropylation (PTFSS3-*b*-PFS1) the -O*H* resonance has completely disappeared and new broad resonances at 4.1, 2.6, and 1,9 ppm corresponding to one oxymethylene and two methylene protons from the attached sulfopropyl groups appear as seen in Figure 2.2.2c.2 b. The sulfopropylated block copolymer with 60 mol% PFS and 78% hydroxyl group conversion was not soluble in DMF and DMSO but could be dissolved in THF/water mixture (1:1 v/v) at room temperature.

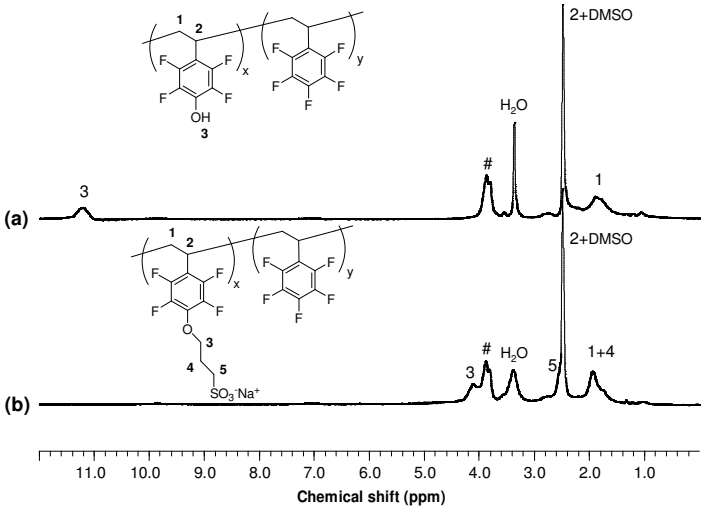


Figure 2.2.2.c.2 ^{1}H NMR spectra in DMSO-d_6 of (a) PTFHS3-*b*-PFS1 and (b) PTFSS3-*b*-PFS1. # is resonance from residual -OCH_3 protons.

2.2.2.d. Preliminary Investigations of Thermal Stability.

The fluorinated copolymers with between 14 and 26 mol% sulfonate groups randomly distributed start to decompose in N_2 above 280 ^oC. However, in the block copolymers the introduction of PFS imparts a higher thermal stability (on the order of 40-80 ^oC) to the sulfonate containing block depending on the PFS content. In fact, two degradation steps can be easily monitored in the TGA trace. The initial degradation step correlates precisely with the original weight of the sulfopropylate groups in the block copolymers.

2.2.3 Oppositely Charged Polyelectrolytes.

Two different synthetic approaches were applied to modify an aromatic polymer backbone containing randomly distributed hydroxyl groups with primary amine or sulfonate pendant groups. The first one involved a Williamson type etherification of the polymer chain with suitable low-molar mass reagents, while the second approach relied on the "click" chemistry[24]. Both methods proved to be highly efficient. As a result polybases and polysulfonates with comparable number and density of functional groups were obtained. This is important in terms of ensuring a complete ionic cross-linking between the two polymers. The cross-linked blends were obtained by mixing the polysulfonate and polybase solutions in dipolar aprotic solvent. Although it was not possible to cast coherent films from the polystyrene-based polymers the described synthetic approach could be used as a general method for the preparation of ionically cross-linked membranes.

The structure of the acid-base blend membrane is presented schematically in Figure 2.2.3.1.

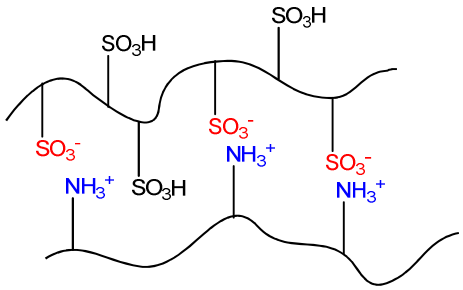


Figure 2.2.3.1. Ionically cross-linked acid-base blend membrane.

2.3 Synthesis of PEM by grafting techniques, work conducted at IRD.

PEM synthesis conducted at IRD.

The overall focus of PEM synthesis at IRD has been to synthesize membranes by grafting techniques involving irradiation by electrons whereby an existing polymer can be modified to conduct protons.

As explained in MS3 several different strategies for PEM synthesis were followed.

a) Traditional grafting. The 'traditional' three-step grafting technique, where the polymer film is irradiated with electrons, grafted and subsequently sulfonated. The apparatus for grafting has been optimized further.

b) Monomers with proton conducting moiety. A grafting technique using monomers, which already contains the sulfonate moiety. With this technique sulfonation, which is very harsh, is avoided.

c) New monomers. A modification of the traditional grafting utilizing monomers, which require alternative treatment in order to become proton conductive.

Traditional grafting

A substantial effort has been devoted to improve grafting whilst maintaining the tensile properties of the original film. Thus the target objective has been to improve conductivity, mechanical properties and electrochemical stability compared to previous membranes.
In MS3 it was recognized that grafting in the surface of the film was not achieved and lack of surface grafting was believed to be associated with the presence of oxygen[25].
The attempts to determine to determine whether exclusion of oxygen would lead to better surface grafting was made in a successive set of experiments.

a) Placing the sample to be irradiated in a polyethylene bag.
b) Placing the sample in a laminated bag consisting of PE/Al/PA (Reducing diffusion of oxygen compared to PE).
c) Sample mounted in a frame resulting in no touching of the sample. The sample and frame was then placed in a bag. Handling of the samples **after** irradiation also evolved from handling in air to (almost total) exclusion of air.
d) Exclusion of air in a flexible, inflatable polyethylene chamber with built-in gloves.
e) Exclusion of air in a glove box.

Find more elaborate description of the efforts to improve surface grafting below.

The preparation of IRD standard-sized membranes has been further optimized. Results are reported below.

Monomers with proton conducting moiety.

The direct incorporation of other proton conducting moieties has been pursued.

New monomers.

The ability to conduct protons at low relative humidity is very attractive. However, this requires new monomers to be developed. Find results below.

2.4 Optimisation of reaction vessel.

The development reported in MS3 resulted in significant improvements of the grafting procedure and ease of handling the films.
Further improvements have been taking place.

Removal of spacers and magnet

The use of spacers and a magnet in the grafting solution chamber complicated the handling and reduced the effective size of the films that could be grafted, see figure 2.4.1.

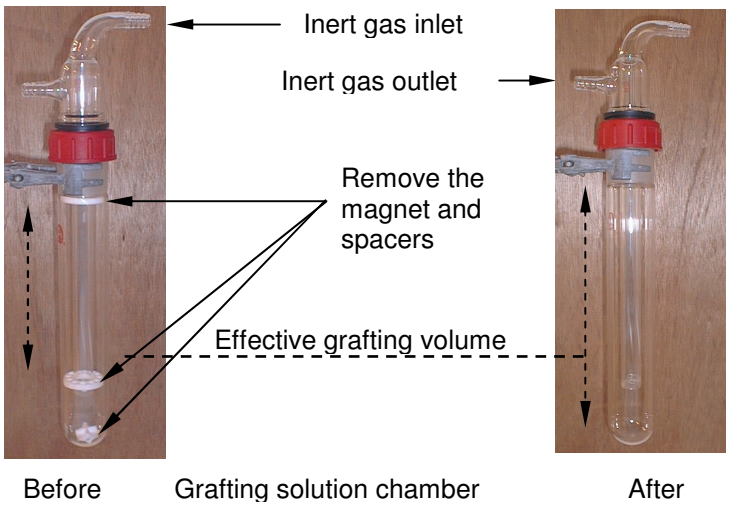


Fig. 2.4.1 Grafting apparatus with designated improvements.

Thus the size of the films may be increased by removing the spacers and the magnet. Furthermore, since the grafting involves significant dimensional changes of the grafted film, it was often found that the spacers put restraints on the swelling leading to grafted films with indents caused by the net. The indents are hard to remove – especially if a cross linker has been used as one of the monomers - the indents cause the film to appear thicker than it actually is and will effect the preparation of the membrane electrode assembly (MEA).
The magnet stirrer was found to be of little importance. The reaction chamber is constantly being flushed with nitrogen, N_2 (g) and the buoyancy of the bubbles from the nitrogen gas ensures thorough mixing of the liquid preventing phase separation of monomers and grafting solution (water and 2-propanol).
The net has been found to be essential in order to keep the films separated while in the reaction chamber. The net ensures an intimate contact with the grafting solution and the monomers preventing problems of monomer diffusion into the film.
Reducing monomer volume
As reported earlier (MS3) the effective volume has been reduced approximately 65 – 70%. The monomer volume has also been decreased from approximately 20% to 15 % without any loss of grafting efficiency. Since the monomers are the most costly components savings in the order of 60 - 70% can be realized.

A model for estimation of production costs has been developed, see figure 2.4.2. The model now handles 3 different substrates (more may be added) and up to 3 different monomers and will check whether added monomer amounts are plentiful enough too prepare a film with a specific grafting level (polymer formation outside film is also taken into account). The model can also account for added costs due to manual labour; however, the costs related to e.g. nitrogen flushing, heating oil bath, cooling condensers etc. have not yet been addressed.
Table 2.6.1 lists the costs associated with different types of fluoropolymer films. To give an idea of the approximate cost the raw cost per batch, the raw cost per m^2, the raw cost per kW (20 membranes per kW assumed) and the cost with 1 labour included are included. The largest reactor at IRD can handles a volume of 2L and labour costs are clearly the most expensive cost driver and automated systems, e.g. roll-to-roll systems, should be considered when designing in larger scale. Clearly the manual handling adds by far most to the overall cost of the membrane. Table 2.4.1 also indicates that is possible produce grafted membrane at a cost (50µ: ~ 30 – 31 €/m^2), which is considerably lower than that of Nafion (50µ: ~ 250 \$/m^2).
Raw material costs have not been negotiated and do leave room for further optimisation of costs. The process developed is not restricted to the types of films mentioned above but is generally applicable to most types of polymer films.

Film type	Raw Cost/batch €/batch	Raw Cost/m^2 €/m^2	Raw cost/kW* €/kW	Labour** incl. €/batch
PVdF	39.57	31.04	12.34	114.57
ETFE	38.00	29.81	11.85	113.00
FEP	41.87	32.81	13.05	116.87

Table 2.4.1 Cost of producing different types of film.

* An IRD 1 kW stack produced with Nafion® requires 18-19 membranes. Here 20 membranes have been used to calculate the cost per kW.

** 1 man-hour is assumed to be required. Labour cost has been set to 75 €/h.

Membrane production cost	**€/m²**	**29.81**
Membrane production cost	**€/kW**	**~ 11.85**

Size & number	Unit		
Length of electrode	m	0.125	
MEA area	m²	0.0156	
Sealing edge	m	0.0075	
Membrane area	m²	0.0176	
Length of film	m	8.5	OK
Width of film	m	0.15	OK
Separator fil thickness	mm	0.5	
No. of membranes per running meter		7.55	
No. of membranes/batch		64	

Substrate			€/batch
Choose substrate			
ETFE		ETFE	
	µm	50	6.38

Monomer			
NB1 Monomer 3 is cross linker			
Monomer 1 MTY	mole	2.05	
Monomer 2 None	mole	0.00	
Monomer 3 DVB	mole	0.18	
Monomer 1 : monomer 2 ratio		0.50	
Monomer volume	L	0.297	OK
M1: MTY	g	242.269	
M2: None	g	0.000	
M3: DVB	g	23.434	
M3: DVB	%	9.67	

Total batch cost			**38.00**

Grafting Batch cost			€/batch
Batch size	L	2	
Degree of grafting, DOG	%	30	
Temperature	°C	65	
Monomer percentage	%	15	
Grafting solution (GS) volume	L	1.700	
Water percentage		45	
Water volume	L	0.765	0.00
IPA volume	L	0.935	6.45
Monomer volume	L	0.300	
M1: MTY	L	0.271	15.63
M2: None	L	0.000	0.00
M3: DVB	L	0.025	2.07

Cleaning solution batch cost			€/batch
Cleaning solution reuse		20	
Toluene	L	2	0.76

Sulfonating solution			€/batch
Sulfonating solution reuse		5	
Sulfonating solution volume	L	2	
CSA percentage	%	0.05	
1,2-dichloroethane	L	1.900	2.91
Chlorosulfonic acid	L	0.100	3.82

Manual labour			€/batch
Labour TAP	h	0	0

Figure 2.4.2 Model developed to predict the costs associated with the production of membrane for FC. Substrate and monomers may be chosen independently from each other and the model checks whether ample amounts of monomers have been added and also for polymer formation outside the film.

Grafting in reduced oxygen atmosphere

Attempts to determine to determine whether exclusion of oxygen would lead to better surface grafting has been made in a successive set of experiments. Experiments were carried out with the grafting apparatus as part of the optimization procedure described above.

a) Placing the sample to be irradiated in a polyethylene bag.
b) Placing the sample in a laminated bag (PE/Al/PA).
c) Sample mounted in a frame and placed in a bag (PE and laminate) – no touching of film condition (initially transfer of film to reaction chamber in air).
d) Like c) but transfer to reaction chamber with minimal exposure to air.

Initially the grafting apparatus was moved to a polyethylene bag with integrated gloves, see figure 2.4.3, (AtmosBag, Sigma Aldrich). During operation/grafting the bag was flushed with nitrogen, N_2 (g). This setup, however, never worked properly due to very limited space,

Fig. 2.4.3 Polyethylene bag with integrated gloves. The snippets at the sides were used for flushing with nitrogen and inlets for electrical cords.

The grafting apparatus (grafting camber and heating plate) was then moved to a glove box. The condenser had to be placed outside the glove box in order to allow for return of condensed monomers and grafting solution, see fig. 2.4.4. The oxygen level of the glove box is continuously monitored and hence the oxygen level can be controlled by flushing with nitrogen, N_2 (g). With this arrangement the oxygen level in the glove box can be controlled and maintained at a level below 0.05%, which is corresponds to a reduction of approximately 400%.

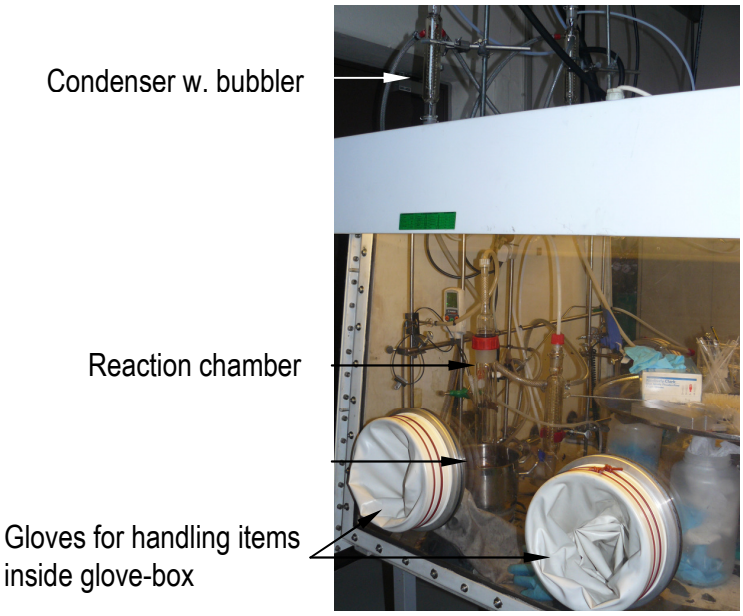


Fig. 2.4.4 Glove box with grafting apparatus.

2.5 PEM synthesis by irradiation, grafting followed by sulfonation.

Pertinent to the synthesis of PEM by this 'traditional' method has been the optimization of the surface graft since it was identified[26] to be a major obstacle to achieve proper conductivity. Two different routes have been followed. Important to both routes has been the aim of improving the electrochemical stability compared to previously developed membranes. Thus the following approaches have been pursued:

1. A synthesis route where the susceptible α-hydrogen in the **polymer**-backbone is replaced by group/atom that is less susceptible for radical attack again with the aim of improving electrochemical stability.
2. A synthesis route where the substituted styrenes are used as monomers. The substituted styrenes do give better chemical stability in a Fentons test (as shown by Mikkel Juul Larsen[27]). The synthesis has involved both experiments with blends of an isomeric mixture of *meta-/para*-methylstyrene and *para-tert*-butylstyrene[28], methylstyrene and methacrylonitrile as well as methylstyrene and *para-tert*-butylstyrene as the only monomer.

2.5.1 Synthesis of PEM with α-methyl containing monomers.

The advantage of preparing proton conducting polymers with the α-hydrogen substituted by an e.g. methyl group is the fact that the α-hydrogen is more prone to extraction by radicals [29, 30], see figure 2.5.1.1.

α-methyl styrene (AMS) and methacrylonitrile (MAN), see figure 2.5.1.2, lack this α-hydrogen and has been chosen based on both electrochemical stability - as well as economic considerations.

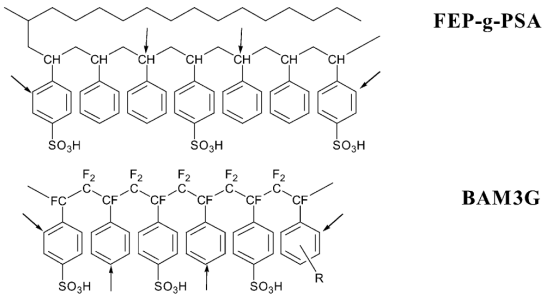


Figure 2.5.1.1 α-hydrogen is more prone to extraction by radicals. The attack of radicals result in polymer cleavage. The figure indicates possible attack sites for this attack.

The use of the co monomer methacrylonitrile stems from the fact that the ceiling temperature of the homopolymer poly-α-methyl styrene is rather low (61°C). At this temperature the polymer formation rate and depolymerisation rate is equal and in order to prevent this depolymerisation methacrylonitrile is being used as co monomer (and because the nitrile group may be used for further chemical derivatisation). The commercial polymer Luran® KR 2556[31] is a copolymer between AMS (70%[w/w]) and MAN (30%[w/w]). In order to ensure good stability of the grafted polymer equimolar amounts of AMS and MAN (app. 60%[w/w] to 35%[w/w] – the rest being cross linker monomer) have been used.
Also divnylbenzene, DVB, is used as a cross linker since all previous fabricated membranes have shown improved the electrochemical stability when DVB is used as cross linker in this synthesis.
As polymer substrates for the grafting reaction the fluoropolymers ETFE (50 µm & 25 µm) and PVdF (50 µm) have been chosen.

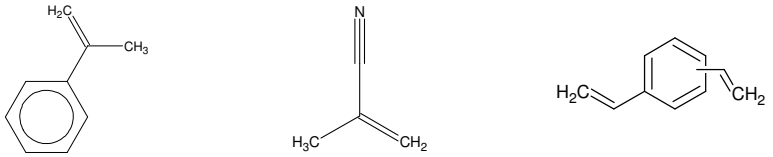


Figure 2.5.1.2 Monomers used for grafting. α-methyl styrene (AMS) and methacrylonitrile (MAN) have no hydrogen atom in alpha position. Divinylbenzene (DVB) is used as a cross linker.

Grafting conditions.
The grafting conditions that have been applied for the styrene/DVB-case have been chosen as a starting point for the synthesis (see appendix A for an Instruction to the grafting procedure):

Irradiation of film:	both sides
Irradiation, dose:	varying
Grafting temperature:	60°C (below ceiling temperature!)
Grafting sol., water/isopropanol ratio:	45/55 (v/v)
Monomer sol., AMS/MAN/DVB ratio:	varying
Inert gas:	N_2

Both grafting- and monomer solutions were flushed with N_2(g) prior to grafting start.

The irradiation of the polymer film were done on both sides in order to ensure a uniform radical distribution throughout the film. In a prior internal work irradiation uniformity has been shown to depend on both the thickness of the film and the accelerating voltage.
The absorbed dose caused by the electron beam is calculated from the radiochromic film B3 from Risø/GEX Corporation. When radiochromic film is exposed to ionising radiation, colouration occurs[32]. This colouration is due to an attenuation of some of the visible light coming through the developed film, resulting in a 'greying'(reddening) of its appearance. The reduction in light passing through the film is a measure of its 'blackness' or 'optical density' (OD). A pivotal assumption in film dosimetry is that the dose to the film is reflected in the resulting optical density of that film. This relationship can be expressed as follows:

$$Optical\ density = \log_{10} \frac{I_0}{I}$$

where I_0 is the light intensity with no film present
I is the light intensity after passing through the film.

Note that since I_0/I has an exponential relationship to the dose, the optical density is appropriately linear with dose.
Since IRD do not have an apparatus for measuring optical density, but do have a scanner, HP OfficeJet 85G. The scanner has been used to measure the optical density of the B3-film. A calibration of dose has been verified against films irradiated at IRD and measured at Risø.

Results

From table 2.5.1.1 the irradiation dose (kGy) and degree of grafting, DOG (%), for both ETFE, FEP and PVdF can bee seen.

Batch	**Dose**	**DOG**	**AMS**	**MAN**	**DVB**
ETFE	kGy	%	g	g	G
ETFE-2007-05-16-2	10.9	21.8	42.76	24.28	3.83
ETFE-2007-05-21-2	16.5	37.0	28.41	16.18	2.67
ETFE-2007-05-22-3	18.4	20.2	28.44	16.11	2.64
ETFE-2007-06-11-1	39.0	63.2	23.63	13.42	2.10
ETFE-2007-06-11-2	37.6	62.0	23.63	13.42	2.10
ETFE-2008-08-21-1	31.7	41.0	23.96	13.62	0.81
ETFE-2008-08-21-2	47.5	65.0	23.96	13.62	0.81
ETFE-2008-08-26-1	29.7	32.4	18.92	12.26	0.72
ETFE-2008-08-26-2	49.2	51.9	18.92	12.26	0.72
ETFE-2008-08-27-1	52.0	39.9	18.93	12.31	0.75
ETFE-2008-08-27-2	66.8	43.1	18.93	12.31	0.75
ETFE-2008-08-27-3	52.0	90.6	23.64	13.42	0.84
ETFE-2008-08-27-4	35.0	100.8	23.64	13.42	0.84
ETFE-2008-09-03-1	37.3	49.3	23.60	13.46	0.82
ETFE-2008-09-03-2	50.5	71.1	23.60	13.46	0.82
ETFE-2008-09-17-1	27.0	23.5	23.63	13.42	0.75
ETFE-2008-09-17-2	15.3	23.2	23.63	13.42	0.75
ETFE-2008-09-22-1	56.7	53.7	23.64	13.43	0.80
ETFE-2008-09-22-2	53.6	58.8	23.64	13.43	0.80
ETFE-2008-09-24-1	13.9	1.1	23.68	13.46	0.77
ETFE-2008-09-24-2	13.9	2.9	23.68	13.46	0.77
ETFE-2008-09-29-1	18.0	5.3	23.69	13.56	0.80
ETFE-2008-09-29-2	23.6	16.7	23.69	13.56	0.80
ETFE-2008-10-02-1	89.4	78.8	23.69	13.45	0.87
ETFE-2008-10-02-2	91.9	31.5	23.69	13.45	0.87
ETFE-2008-10-08-1	45.9	54.8	23.76	13.43	0.80
ETFE-2008-10-08-2	54.8	55.4	23.76	13.43	0.80

Batch	**Dose**	**DOG**	**AMS**	**MAN**	**DVB**
FEP	kGy	%	g	g	g
FEP-2007-05-16-1	11.4	0.8	42.76	24.28	3.83
FEP-2007-05-21-1	16.6	1.6	28.41	16.18	2.67
FEP-2007-06-11-3	38.8	0.9	23.63	13.42	2.10
FEP-2007-06-11-4	37.9	25.2	23.63	13.42	2.10
FEP-2007-06-28-1	25.2	9.0	23.63	13.42	2.10
FEP-2007-06-28-2	41.5	3.0	23.63	13.42	2.10
PVdF	kGy	%	g	g	G
PVDF-2007-06-28-1	21.5	31.2	23.63	13.42	2.10
PVDF-2007-06-28-2	21.4	27.0	23.63	13.42	2.10
PVDF-2009-01-20-1	89.0	2.9	23.85	13.43	2.04
PVDF-2009-01-20-2	87.2	130.5	23.85	13.43	2.04

Table 2.5.1.1 Listing of batches grafted with AMS, MAN and DVB.

Generally the grafting with AMS, MAN and DVB never worked optimally. There are several reasons for this:

1 The grafting temperature is probably too close to the ceiling temperature causing de-polymerisation close to the rate of polymerisation. Lowering the grafting temperature would have been obvious; however, this would prolong grafting sessions to unacceptable lengths.

2 Prediction of the grafting levels were poor, see figure 2.5.1.3. Stable grafting and prediction of grafting level is possible with other types of monomers as will be shown below in section 3.3.2. There is probably an effect caused by the type of film, however, this has not been studied extensively.

3 Films had a tendency to adopt the shape of the net, which did not disappear after sulfonation. Choosing a finer net just caused the indents to be finer. The indents in the film did cause problems when trying to prepare a Membrane Electrode Assembly (MEA), since good contact between the electrode and the membrane was hard to obtain.

4 Grafted film tended to be fragile. After sulfonation the films become even more fragile making the preparation of the MEA very problematic since the film had a tendency to crack.

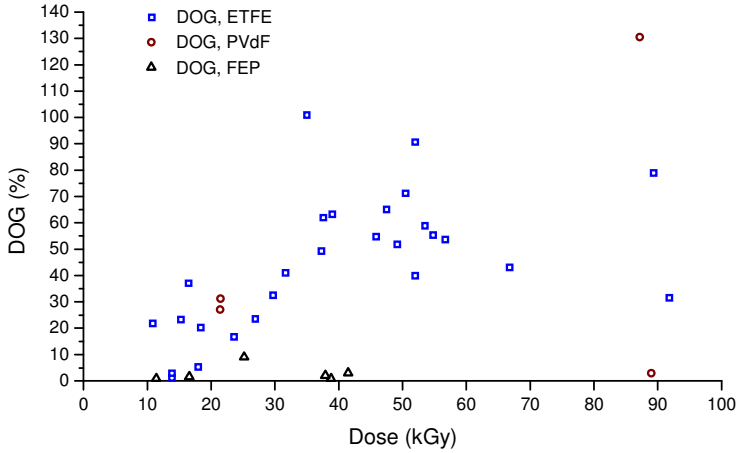


Figure 2.5.1.3 DOG as a function of dose. For all substrates the correlation, R^2, is poor.

In order to determine the DOG a procedure for drying the membranes after extraction (see appendix A) has been developed. Normally the membranes are left in vacuum for approximately 1 hour at 80°C. Accidentally some membranes were left for about 1 week at 80°C (without vacuum) after having determined their DOG. It turned out the membranes had lost weight during this period and a residue was found below the membranes on a sheet of PET-film (Hostaphan). An IR-spectrum of the residue as well as the PET-film did reveal a positive identification of a mixture of polymer fragments of α-methylstyrene and methacrylonitrile (and Hostaphan), see fig. 2.5.1.4.
From literature[29,33] membranes with AMS, MAN and DVB have been shown to work for at least 1000 hours; however, no reports of membranes leaking grafts have been identified, but if the membranes are not able to withstand temperatures of at least 70°C to 80°C there is no future for that membrane. Consequently all development with α-methylstyrene were abandoned.

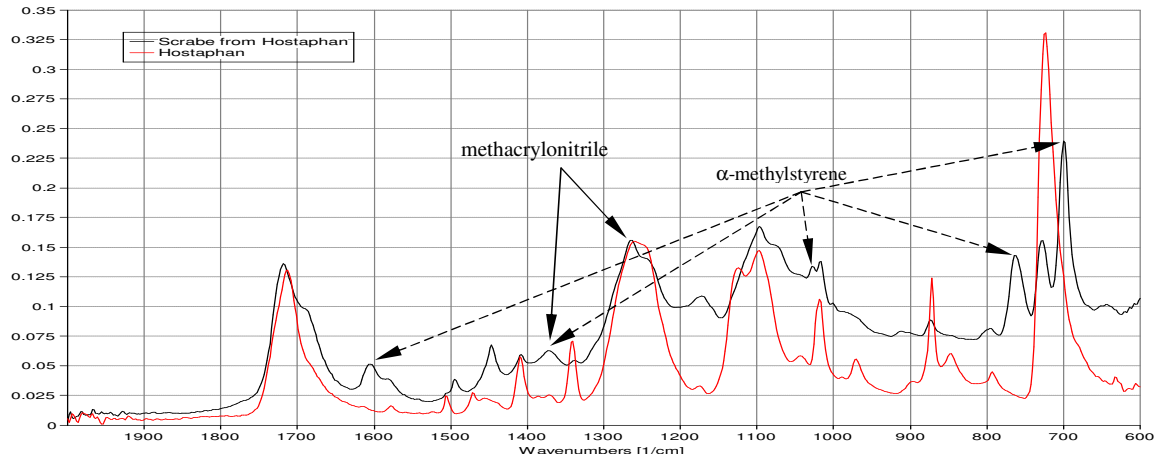
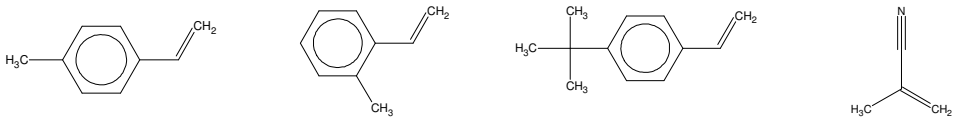


Figure 2.5.1.4 ATR-IR-spectra of residue from Hostaphan film.

2.5.2 Grafting with alkyl substituted styrenes

The reasons for using substituted styrenes are similar to α-methylstyrene. The grafts with methyl styrene (MTY) and *tert*-butyl styrene have shown improved stability in Fentons test [27,28]. Methacrylonitrile (MAN) have been applied as a co-monomer to MTY/TBY for the same reasons, it provides better chemical stability, and all the monomers are affordable in price implying that membranes may be produced at an affordable cost (see section 2.6).



MTY MTY TBY MAN

Figure 2.5.2.1 Two isomers, *meta*- and *para*-methylstyrene (MTY), *para-tert*-butylstyrene (TBY) and methacrylonitrile (MAN).

Grafting conditions.

The grafting conditions that have been applied for the substituted styrene/DVB-case have been chosen as a starting point for the synthesis (see appendix A for an Instruction to the grafting procedure):

Irradiation:	both sides
Irradiation, dose:	varying
Grafting temperature:	65°C
Grafting sol., water/isopropanol ratio:	45/55 (v/v)
Monomer sol., MTY/TBY/MAN ratio:	varying
Inert gas:	N_2

Both grafting- and monomer solutions were flushed with N_2(g) prior to grafting start.

Dose is measured as described in section 2.5.1.

In table 2.5.2.1 below is a listing of grafting sessions with different starting conditions.

Batch	**Dose**	**DOG**	**DVB**	**MTY**	**TBY**	**MAN**
ETFE	kGy	%	g	G	g	G
ETFE-2007-10-23-1	25.4	46.61	1.02	24.50	24.01	0.00
ETFE-2007-10-23-2	26.0	48.16	1.02	24.50	24.01	0.00
ETFE-2007-10-23-3	28.2	39.38	1.02	24.50	24.01	0.00
ETFE-2007-10-23-4	26.9	43.98	1.02	24.50	24.01	0.00
ETFE-2007-11-01-1	17.4	26.07	6.02	29.50	29.01	0.00
ETFE-2007-11-01-2	18.3	131.54	6.02	29.50	29.01	0.00
ETFE-2007-11-01-3	17.0	101.83	6.02	29.50	29.01	0.00
ETFE-2007-11-01-4	16.0	82.22	6.02	29.50	29.01	0.00
ETFE-2007-11-06-1	11.4	22.04	1.09	24.61	24.30	0.00
ETFE-2007-11-06-2	11.1	19.20	1.09	24.61	24.30	0.00
ETFE-2007-11-06-3	12.2	25.84	1.09	24.61	24.30	0.00
ETFE-2007-11-06-4	21.4	38.82	1.09	24.61	24.30	0.00
ETFE-2009-04-22-2	10.0	78.48	0.00	39.00	0.00	0.00
ETFE-2009-04-22-4	14.6	93.94	0.00	39.00	0.00	0.00
ETFE-2009-04-28-2	5.7	59.55	0.00	39.00	0.00	0.00
ETFE-2009-04-28-4	6.1	57.73	0.00	39.00	0.00	0.00
PVdF						

Batch	Dose	DOG	DVB	MTY	TBY	MAN
PVDF-2009-03-09-2	50.6	97.07	0.00	27.83	0.00	16.20
PVDF-2009-03-09-3	43.6	98.48	0.00	27.83	0.00	16.20
PVDF-2009-03-10-1	51.8	105.45	0.00	27.83	0.00	16.20
PVDF-2009-03-10-2	48.4	103.98	0.00	27.83	0.00	16.20
PVDF-2009-03-10-3	53.4	103.88	0.00	27.83	0.00	16.20
PVDF-2009-03-11-1	55.3	108.90	0.00	27.95	0.00	15.89
PVDF-2009-03-11-2	49.1	103.79	0.00	27.95	0.00	15.89
PVDF-2009-03-11-3	48.2	106.45	0.00	27.95	0.00	15.89
PVDF-2009-03-11-4	39.6	106.63	0.00	27.95	0.00	15.89
PVDF-2009-03-18-1	66.6	72.39	0.00	24.83	0.00	14.09
PVDF-2009-03-18-2	54.9	104.25	0.00	24.83	0.00	14.09
PVDF-2009-03-18-3	51.8	86.76	0.00	24.83	0.00	14.09
PVDF-2009-03-18-4	51.5	100.16	0.00	24.83	0.00	14.09
PVDF-2009-03-18-5	51.0	106.56	0.00	24.83	0.00	14.09
PVDF-2009-03-18-6	48.0	103.66	0.00	24.83	0.00	14.09
PVDF-2009-03-19-1	21.5	78.03	0.00	24.83	0.00	14.09
PVDF-2009-03-19-2	24.5	78.19	0.00	24.83	0.00	14.09
PVDF-2009-03-19-3	28.0	75.46	0.00	24.83	0.00	14.09
PVDF-2009-03-19-4	20.7	75.28	0.00	24.83	0.00	14.09
PVDF-2009-03-23-1	37.8	81.03	0.00	24.83	0.00	14.09
PVDF-2009-03-23-2	31.5	77.19	0.00	24.83	0.00	14.09
PVDF-2009-03-23-3	31.8	78.98	0.00	24.83	0.00	14.09
PVDF-2009-03-23-4	40.0	77.88	0.00	24.83	0.00	14.09
PVDF-2009-03-24-1	33.7	82.56	0.00	39.00	0.00	0.00
PVDF-2009-03-24-2	27.9	88.94	0.00	39.00	0.00	0.00
PVDF-2009-03-24-3	25.7	93.52	0.00	39.00	0.00	0.00
PVDF-2009-03-24-4	30.8	92.01	0.00	39.00	0.00	0.00
PVDF-2009-03-25-1	21.5	85.57	0.00	39.00	0.00	0.00
PVDF-2009-03-25-2	21.2	82.56	0.00	39.00	0.00	0.00
PVDF-2009-03-25-3	19.2	89.20	0.00	39.00	0.00	0.00
PVDF-2009-03-25-4	20.1	85.68	0.00	39.00	0.00	0.00
PVDF-2009-04-22-1	9.9	52.23	0.00	39.00	0.00	0.00
PVDF-2009-04-22-3	10.5	60.07	0.00	39.00	0.00	0.00
PVDF-2009-04-28-1	5.8	33.57	0.00	39.00	0.00	0.00
PVDF-2009-04-28-3	5.7	33.75	0.00	39.00	0.00	0.00
PVDF-2009-02-12-1	90.1	1.69	0.00	29.57	0.00	8.45
PVDF-2009-02-12-2	88.9	1.71	0.00	29.57	0.00	8.45
PVDF-2009-02-27-1	81.1	25.79	0.00	29.55	0.00	8.41
PVDF-2009-02-12-3	92.2	31.61	0.00	0.00	32.31	6.73
PVDF-2009-02-12-4	92.1	20.92	0.00	0.00	32.31	6.73
PVDF-2009-02-24-3	81.8	5.23	0.00	0.00	27.27	11.40
PVDF-2009-02-24-4	74.6	0.11	0.00	0.00	27.27	11.40
PVDF-2009-02-27-2	92.2	0.42	0.00	0.00	32.06	6.71
PVDF-2009-03-03-2	74.9	1.02	0.00	0.00	36.88	0.00
PVDF-2009-03-04-2	51.0	56.77	0.00	0.00	0.00	38.96
PVDF-2009-03-04-3	51.0	54.46	0.00	0.00	0.00	38.96

Table 2.5.2.1 Listing of batches grafted with MTY, TBY, MAN and DVB. The part below the fat, marked line is batches with unanticipated grafting attempts.

Prior to rising the temperature prediction of DOG was a matter of guessing. As pointed out by T. Rager[34,35] the time until the grafting front has progressed to the center of the film is mainly affected by the film thickness and the reaction temperature the grafting. Indeed the temperature does significantly affect the grafting result, however the very poor grafting results with TBY (see below the fat, marked line in table 2.5.2.1) indicates that other factors influence the grafting result.

The reaction rates for polymerization and radical recombination are related. From figure 2.5.2.1 the fitted line indicates that with increased dose the recombination rate of the generated radical sites increase while the grafting result does not increase linearly with dose. As can be seen from figure 2.5.2.1 the effect of increasing the irradiation dose follows an exponential decay that is the effect of increasing dose is counter compensated by an increase in recombination of radicals within the film.
The reasonable correlation between irradiation dose and DOG should not, however, encourage the use of high doses in order to obtain high grafting levels. As a general rule one should try to minimise dose thus minimising the damage caused by the irradiation inside the film. In this respect it may be (justifiably) argued that the irradiation dose used have been excessively high. The high doses were used at a time when α-methylstyrene were investigated as a monomer and no correlation was found. As it turned out good grafting results with MTY can be achieved.

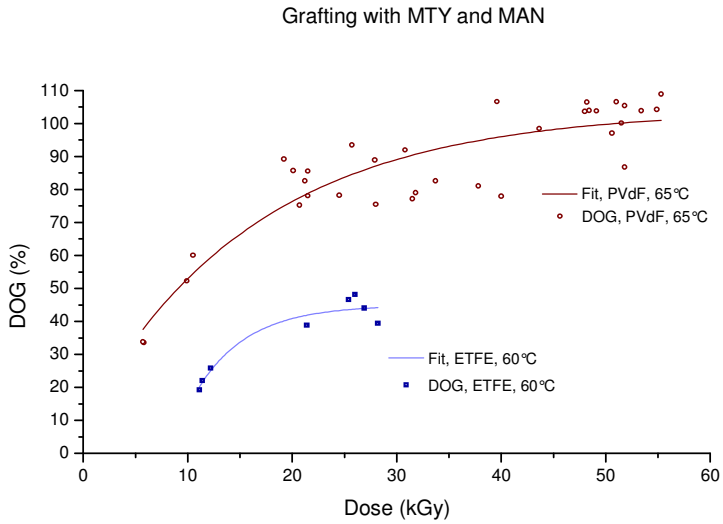


Figure 2.5.2.1 Degree of grafting, DOG, as a function of irradiated dose for PVdF and ETFE substrates

The prediction of DOG can be estimated to a certain extent[34]. However, for both PVdF and ETFE there seems to be a threshold value below which grafting does not follow the same kinetics. The phenomena was also noticed by M.J. Larsen[27], however, the reason for this behaviour is currently not understood.
One thing not noticed by M.J. Larsen was the fact that *tert*-p-butylstyrene does not graft at all (see below the fat, marked line in table 2.5.2.1). When using MTY as the only monomer both PVdF and ETFE grafts according to figure 2.5.2.1. Using only TBY results in no or very little grafting while using a mixture of TBY and MAN or MTY results in moderate grafting. Raising temperature to 70°C does not improve grafting of TBY. From these facts it is very likely that mixtures of MTY/MAN and TBY/MAN only results in grafting of MTY and/or MAN. Some current hypothesises are that either TBY is too bulky or the graft 'closes' the surface for entrance of TBY into the bulk of the film – in both cases TBY is too bulky.

There is a small drawback of increasing the temperature, since polymerisation outside the film (in the grafting solution) increases exponentially with temperature. Thus the monomers will have a greater tendency to polymerise outside the film when increasing the temperature, however, if the kinetics for e.g. methylstyrene is lower or comparable to styrene (which has been assumed in this work) this has not caused any problematic increase in polymerisation in the grafting solution. One way of suppressing the autopolymerisation in the grafting solution

is to ad a small concentration of a mineral acid to the solution[36]. This approach is reported to increase the grafting rate, but have not been investigated in this work, however this approach will be tested in a forthcoming project.

2.5.3 Grafting with sulfonated monomers.

In order to avoid the drawbacks of the post-sulfonation method[37, 38] sulfonated monomers can be used to graft polymer films. Post-sulfonating is a harsh chemical treatment that not only sulfonates the graft but also cuts the backbone polymer into smaller pieces and introduces attack sites for later radical decomposition.
Different sulfonated monomers have been tested, see figure 2.5.3.1, namely 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS). Vinylsulfonate, (VS), Styrenesulfonate, (SS). Since radical polymerisation is impeded by the sulfonic acid moiety[39] the acid functionality can be temporarily removed by reacting the acid with a suitable base. Also the reaction with a base has the purpose of 'disguising' the polar nature of the sulfonate group. With AMPS both pyridine and tributylamine has been tested. With vinylsulfonate and styrenesulfonate the monomers have been tested as sodium salts.

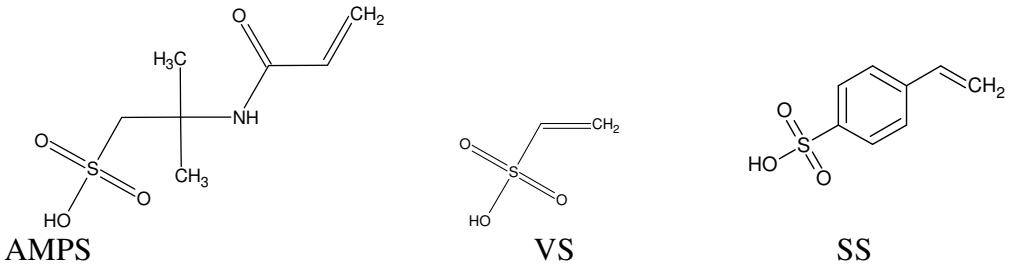


Figure 2.5.3.1 Different sulfonated monomers. 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS). Vinylsulfonate, (VS), Styrenesulfonate, (SS).

Several different grafting approaches have been tested.
The usual 'standard' way of pre-irradiation followed by immersion and grafting proved futile. The sulfonated monomers are simply too polar and does not penetrate into the substrate. The use of non-polar solvents as a grafting solution does not work either since the monomers cannot be dissolved in these solvents.
Another approach where PVdF was dissolved together with the monomers (in an aprotic solvent) after which the solution was irradiated also proved futile. Some polymerisation was observed, however, it is not a grafting, which takes place. The idea of creating 'semi'-stable radicals inside the polymer film onto which the polymerisation can take place becomes obsolete when dissolving the polymer – in a dissolved polymer the generated radicals are free to move and react, which they do. Thus the sulfonated polymer did **not** graft to the backbone polymer and the two polymers phase separate after removal of the solvent.

The attempts of directly introducing the sulfonate group via the pre-irradiation method was terminated (but can be realised by other polymerisation techniques).

2.5.4 Concluding remarks on grafting

The use of a cross linker to increase electrochemical stability has been documented[40,41], however the mechanical properties of the membrane becomes less desirable with increased amounts of cross-linker. In general the tensile modulus and strength increase with increased levels of cross linker and the swelling and toughness decrease – the membrane becomes brittle. Also conductivity of the membrane is closely related to the uptake of water that is

with swelling and hence the use cross-linker. When deciding on the use of increased levels of cross-linker it has to be recognised that this reduces the conductivity and yields poorer mechanical properties. The handling is a problem that has grown more acute when preparing membranes of standard IRD size. After sulfonation the membranes are very brittle and handling in dry state is often associated with cracking making the membranes useless for fuel cell applications since gas crossover occur.
In order to test whether membrane properties can be improved and the problem of brittle membranes circumvented it was decided to use the cross-linker in a later stage of the membrane fabrication process. The brittleness of the membrane is an inherent property related to the grafted material thus in order to stabilise the membrane it was decided to investigate the possibility of using a (polymer) matrix to impart mechanical stability. This implies that the grafted membrane has to be dissolved and recast onto the matrix and hence the cross-linker cannot be used in the initial grafting step. The approach of dissolving and recasting the grafted (and sulfonated) membrane opens for the possibility to formulate with other additives in order to impart e.g. better durability with respect to radical attack, which is known to be an inherent problem with (styrene) grafted membranes.

A matrix for the stabilisation of the grafted, sulfonated material has been identified. Solupor®, produced by Lydall Solutech (formerly DSM Solutech), is an Ultra High Molecular Weight PolyEthylene, UHMWPE, with high porosity and good tensile properties. The thermal properties of polyethylene, however, restricts the use of this matrix to temperatures below 80°C and therefore the search for similar porous materials with better thermal properties is still ongoing (and will be continued in a project following this).

It is possible to dissolve the grafted, sulfonated membrane in an aprotic solvent. N-methyl-2-pyrrolidone has been used. However, in order to dissolve the polymer, very low concentrations of the grafted membrane has had to be used, which unfortunately afterwards requires many recasts/impregnations in order to produce a useful membrane. It turned out that the final recast membrane had inadequate properties – the solution had poor wetting properties. The choice of solvent is important since good wetting is a prerequisite for good membrane properties thus other aprotic solvents have to be considered.

It has been noticed that the solution is gradually lowering the viscosity upon standing. The reason for this is not clear, however, this opens up for the possibility of removing the solvent by evaporation enabling for fewer recasting operations.

2.5.5 Sulfonation

The sulfonation of the grafted film relies heavily on the post sulfonation method that utilises nucleophilic agents, which substitutes into the aromatic ring. Sulfonating agents can be[28] e.g. direct chlorosulfonic acid, chlorosulfonic acid via a silylating agent , concentrated sulphuric acid, sulphur trioxide and/or oleum and acetyl sulphate. In this project three[27] (3) methods have been tested direct chlorosulfonic acid, chlorosulfonic acid via the silylating method and the acetyl sulphate method. The two latter methods have been tested in order to establish whether a more gentle sulfonation method could be established since the direct addition of chlorosulfonic acid is recognised as one of the 'weak' processes leading to chain scission of the grafts[42]. However direct addition of chlorosulfonic acid has been used in this project, since it is fast and reaches high levels of sulfonation, which was not always the case the two latter methods.
The procedure involves:
Sulfonation solvent: 1,2-dichloroethane, $C_2H_6Cl_2$.
Sulfonation agent: chlorosulfonic acid, $ClHSO_3$.

Sulfonating temperature: ambient
Duration of sulfonation: 4 hours

Below, in table 2.5.5.1, are some results for the grafting.

Batch	DOG (%)	DOS[1] (%)	IEC (meq/g)	DOS from IEC (%)	Monomers
ETFE					
ETFE-2007-06-11-2	19.20	115.25			AMS/MAN/DVB
ETFE-2007-10-23-2	48.16	328.77			MTY/TBY/DVB
ETFE-2007-10-23-3	39.38	361.96			MTY/TBY/DVB
ETFE-2007-10-23-4	43.98	446.64			MTY/TBY/DVB
ETFE-2009-04-22-2	78.48	122.00			MTY
ETFE-2009-04-22-4	93.94	127.56			MTY
ETFE-2009-04-28-2	59.55	152.20	2.06	90.71	MTY
ETFE-2009-04-28-4	57.73	217.07	2.09	104.14	MTY
PVdF					
PVDF-2009-01-20-2	130.51	42.96			AMS/MAN
PVDF-2009-01-20-4	131.38	53.29			MTY/MAN
PVDF-2009-03-03-1	105.29	67.78			MTY/MAN
PVDF-2009-03-04-2	56.77	48.76	1.67	37.48	MAN
PVDF-2009-03-04-3	54.46	48.62	1.50	34.47	MAN
PVDF-2009-03-19-1	78.03	48.97	1.79	44.94	MTY/MAN
PVDF-2009-03-19-2	78.19	51.31			MTY/MAN
PVDF-2009-03-19-3	75.46	52.26	1.81	46.75	MTY/MAN
PVDF-2009-03-19-4	75.28	51.41			MTY/MAN
PVDF-2009-03-23-1	81.03	47.93	1.77	43.47	MTY/MAN
PVDF-2009-03-23-2	77.19	52.06			MTY/MAN
PVDF-2009-03-23-3	78.98	50.49	1.89	47.48	MTY/MAN
PVDF-2009-03-23-4	77.88	49.64			MTY/MAN
PVDF-2009-03-24-1	82.56	96.89	2.22	75.31	MTY
PVDF-2009-03-24-2	88.94	87.45	2.23	71.95	MTY
PVDF-2009-03-24-3	93.52	76.81	2.11	64.84	MTY
PVDF-2009-03-24-4	92.01	87.96	2.18	69.24	MTY
PVDF-2009-03-25-1	85.57	90.13	2.22	73.02	MTY
PVDF-2009-03-25-2	82.56	86.36			MTY
PVDF-2009-03-25-3	89.20	87.93	2.24	72.23	MTY
PVDF-2009-03-25-4	85.68	88.18			MTY
PVDF-2009-04-22-1	52.23	125.64			MTY
PVDF-2009-04-22-3	60.07	120.22			MTY
PVDF-2009-04-28-1	33.57	187.40	1.60	99.47	MTY
PVDF-2009-04-28-3	33.75	216.48	1.32	85.07	MTY

Table 2.5.5.1 Listing of batches grafted with AMS, MTY, TBY, MAN and DVB. The grey parts of the table indicates unusual results.

In order to calculate the degree of sulfonation, DOS, one has to know the number of structural units, N_1, that has been sulfonated and the total number of structural units that can be sulfonated, N_2[43]. The DOS can then be calculated from the formula 1)

$$DOS = \frac{N_1}{N_2} \cdot 100\ (\%) \qquad 1)$$

NB!
Formula 1) is a simplification of the more correct calculation of the DOS. If the number structural units containing the sulfonate group (N_1) as well as the number of structural units without (N_2)are known DOS may be calculated from 2)

$$DOS = \frac{N_1}{N_1 + N_2} \cdot 100\ (\%) \qquad 2)$$

Originally the DOS, has been calculated by mass determinations of the sulfonated film. This requires careful drying and fast determination of the mass of the dried film before it soaks up any water vapour from the air. The DOS may then be calculated according to 3)

where:
m_s: mass of sulfonated (dried) film
m_g: mass of grafted (dried) film
m_o: mass of virgin (dried) film
M_{SA}: mass of sulfonate group
M_{avg}: average mass of monomer composition

$$\frac{\left(\frac{m_s - m_g}{M_{SA}}\right)}{\left(\frac{m_g - m_o}{M_{avg}}\right)} \cdot 100\ (\%) \qquad 3)$$

M_{avg} is the average molecular weight of the monomers in the grafting solution. By using M_{avg} it assumed that the grafting proceed with statistically the same distribution of monomers in the grafted film. The distribution of monomers in the film has been investigated by M. J Larsen[27] and H.-P Brack[44] and it cannot be assumed that the same distribution is found in the grafted membrane, however, with new monomers the distribution in the film has not been investigated.
One drawback of the DOS-determination is the method sensitivity to water vapour since the membranes are very hygroscopic – once dried, they will start to 'soak' water vapour from the air immediately after exposure to the air and hence be susceptible misleading DOS determination.
The DOS may also be calculated from the Ion Exchange Capacity, IEC, of the polymer film. In this project the IEC has been determined according to ASTM D-7131-05, 'Determination of Ion Exchange Capacity (IEC) in Grafted Battery Separator'. DOS can then be calculated according to 4)

where:
m_s: mass of sulfonated (dried) film
m_g: mass of grafted (dried) film
m_o: mass of virgin (dried) film
M_{avg}: average mass of monomer composition

$$\frac{0.001 \cdot \mathrm{IEC}}{\left(\frac{m_g - m_o}{M_{avg}}\right) \Big/ m_s} \cdot 100\ (\%) \qquad 4)$$

Although it may be argued that using IEC is prone to the same error (uptake of water while weighing sample) it generally gives results of better quality than the results obtained from formula 3). As can be seen from figure 2.5.5.1 the DOS calculated by titration measurements (IEC) always give results that are lower compared to mass determinations. Also DOS determined by IEC rarely yield results larger than 100% indicating that no more than 1 sulfonate group has been substituted in the aromatic ring (which is not common considering the fact that the sulfonate group is deactivating with respect to further substitution).
In some cases almost 100% sulfonation of grafted material occurs whereas in others it is far from this. In figure 2.5.5.2 the DOG is compared to the DOS. The highly grafted material has relatively low DOS. It appears that high DOG is associated with low DOS. This trend seems to be consistent and it is interesting that samples irradiated with high dose have low degree of sulfonation indicating that the samples have undergone of course a high grafting but also a high degree of recombination, that is radicals annihilate each other by recombining, with the result that the polymer film becomes less permeable to sulfonation, see figure 2.5.5.3. Thus, there are several good reasons to use low doses when irradiating the polymer

film. Low doses reduces the damage to the polymer segments within the film and low doses increase the sulfonation yield.

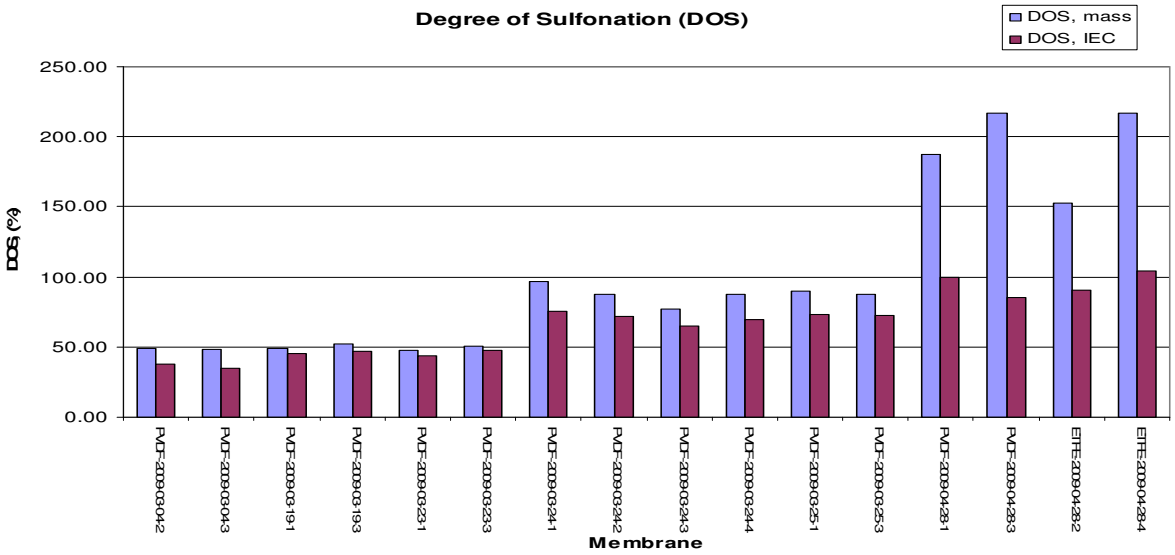


Figure 2.5.5.1 Degree of sulfonation, DOS (%), determined by weighing (mass) and by titration (Ion Exchange Capacity [IEC]) for PVdF and ETFE substrates.

The IEC determination reveals another important issue related to the sulfonation. An average molecular weight per sulfonate group can be determined from the IEC-value:

$$M_{Avg,Sulfo} = \frac{1000}{IEC} \qquad 5)$$

See table 4.1.2 for the calculated average molecular weights.
Compared to Nafion®, which has an IEC ≈ 0.91, the IEC of most of the synthesised membranes are higher resulting in good conductivities. However, this is accompanied with a higher solubility in water and the polymers are close to being water soluble. In a FC the transport of protons is associated with a transport of water, which ultimately will dilute the sulfonated polymer as the FC is operated. The typical way to circumvent this problem has been to cross link the grafted polymer, however, if the cross linker also is prone to sulfonation (and attack of radicals) this will only postpone the dilution effect. The use of cross linker should be accompanied by an 'inert' comonomer when grafting and will be investigated in a following project.

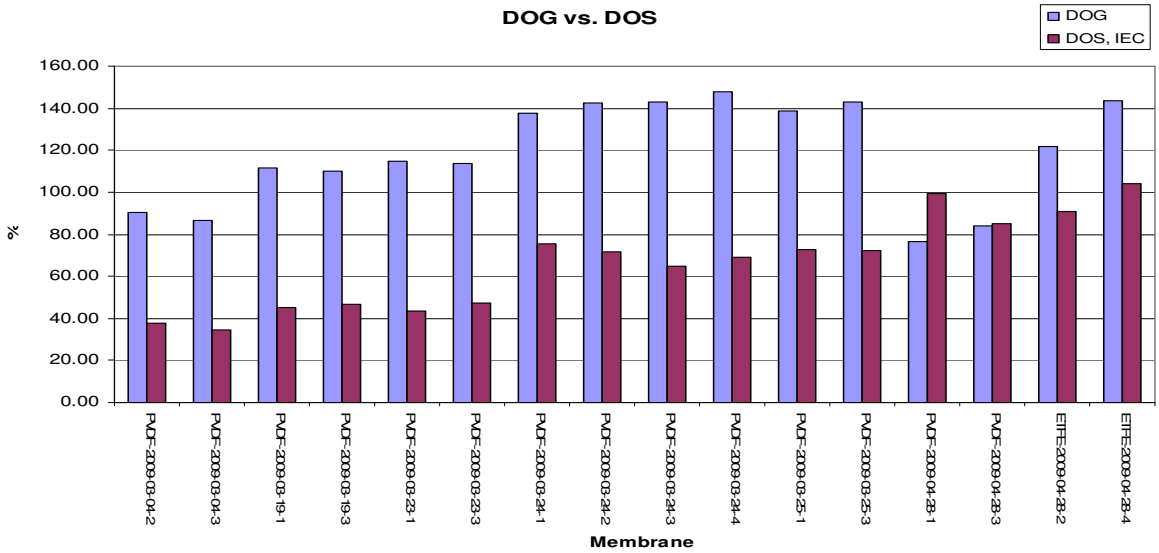


Figure 2.5.5.2 Degree of sulfonation, DOS IEC (%), compared to degree of grafting, DOG, (%).

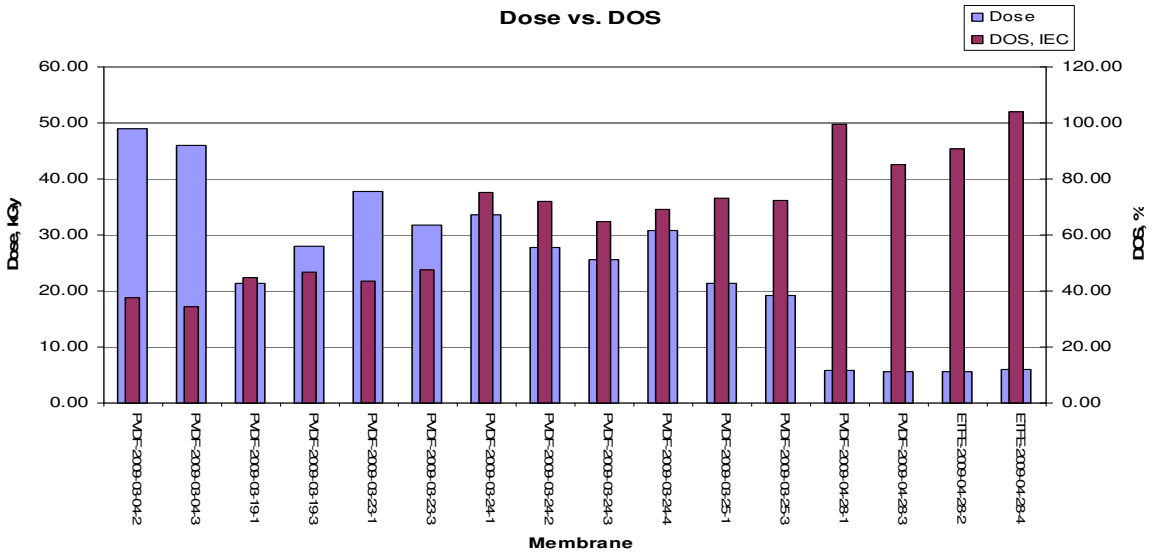


Figure 2.5.5.3 Degree of sulfonation, DOS, IEC (%), compared to irradiation dose (kGy).

After sulfonation the membranes become brittle – especially when dry. The brittleness is a big problem since the handling of the membranes becomes problematic. Normally procedures for preparing an fuel cell (MEA) involves handling the membrane in a relatively dry state and it has become obvious that sulfonated membranes cannot be handled without introducing cracks, which causes gas crossover in the fuel cell.
As can be seen from table 2.5.5.1 a large number of the membranes have been grafted without the use of a cross-linker, since the use of a cross-linker would prohibit the dissolution of the membrane. As noted under the grafting section the plan is to recast the dissolved membrane within a stabilising matrix. The idea is that the recasting process will redistribute the grafts in a more suitable manner, such that the membrane becomes less brittle.
It is possible to dissolve the grafted, sulfonated membranes, however, the concentration is less than 1% making the recasting process unduly long. Upon standing it has been noticed

that the viscosity of the solution becomes lower indicating that the polymer disentangles and probably also reacts at the sulfonic acid group. This means that the concentration may be augmented and the recasting process becomes viable. Another implication, which has not yet been investigated, is that it may be beneficial to react the sulfonic acid group when dissolving the grafted, sulfonated polymer. As noted earlier the dissolution opens up for adding both cross-linker and e.g. radical scavengers to the solution thus achieving better durability afterwards.

Membranes grafted with *only* methacrylonitrile (PVDF-2009-03-04-2 and -3) can be sulfonated and show excellent conductivities (see chapter 4).
The nature of the sulfonation is not entirely clear – in the FTIR-ATR spectrum there are indications to the presence of a sulfonic acid group see figure 2.5.5.4, however, is the sulfonation a substitution of the nitrile group or only of the nitrogen or is it an addition to the nitrile group producing an amidosulfonic acid group? The inserted spectrum, showing the transmission from 2400 – 1850 cm^{-1} does not indicate any presence of a nitrile group, however, the grafting in the surface layer of the polymer film is (by now) known to be poor, which means that the nitrile group may have reacted.
The sulfonation is not complete (~50%) thus even better physical properties may result from further optimisation. The grafted polymer should have a better stability towards radical attack at the α-position compared to styrene (which were the originally the intention with α-methylstyrene/methacrylonitrile).

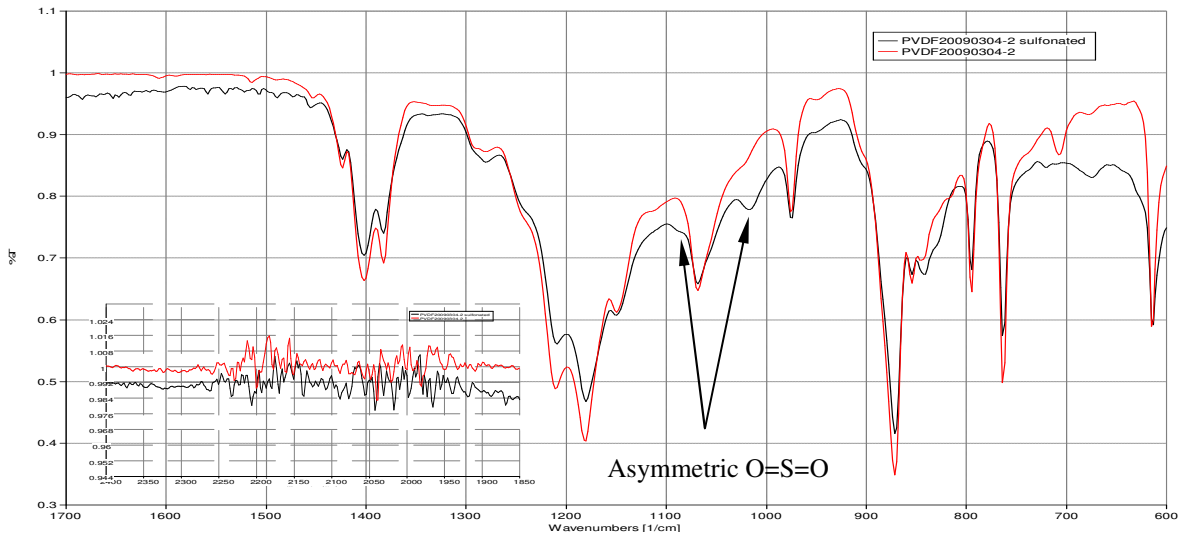


Figure 2.5.5.4 FTIR-ATR spectrum of PVdF grafted with methacrylonitrile. The inserted spectrum show no sign of a nitrile goup.

As opposed to the grafting no clear substrate effect on the sulfonation has been detected.

2.6 Conclusion.

Synthesis from constituent monomers – work made at DPC.
A novel concept for preparation of sulfonate containing fluorinated block copolystyrenes have been developed based on initial ATRP of fluorinated styrene monomers. The strategy depends on well defined macrointiators that after conversion to block copolymers can be post functionalized in two steps with propylsulfonate groups in different ratios. Preliminary thermal investigations have demonstrated that addition of a PFS block to the sulfonate containing block improves the materials' thermal stability.
Synthesis by grafting methods.

The synthesis of fuel cell membranes via radiation grafting can be done at a reasonable cost projected to be approximately 30 – 35 €/m^2 in raw materials cost. This cost most certainly can be optimised and reduced further.
The synthesis of FC membrane with optimised chemical stability proved futile – considerable effort has been put into bringing this membrane to work. α-methyl styrene is not a suitable monomer for FC membranes. The monomer does not graft in a predictable way and the co-polymer of α-methyl styrene and methacrylonitrile is not stable at ordinary FC operation temperatures.

2.7 Future work

A novel concept for preparation of sulfonate containing fluorinated block copolystyrenes have been developed based on initial ATRP of fluorinated styrene monomers. The strategy depends on well defined macrointiators that after conversion to block copolymers can be post functionalized in two steps with propylsulfonate groups in different ratios. Preliminary thermal investigations have demonstrated that addition of a PFS block to the sulfonate containing block improves the materials' thermal stability.

FC membranes with methyl styrene, which also provides better chemical stability than styrene, can be synthesised with good yields. The membranes, however, are very brittle after sulfonation even without cross-linker and cannot be used. A strategy where the grafted, sulfonated membrane is dissolved and later recast into a matrix giving good tensile properties has been followed. Currently the concentration of the solution is too low for practical recasting operations, however, it has been noted that the viscosity of solution becomes lower upon standing indicating that solutions with higher concentrations are possible. The recasting process allows for addition of e.g. cross-linkers and radical scavengers, which ultimately improves the durability of the FC membrane.
The use of co-monomers in order to incorporate inert spacers and reduce solubility also needs to be investigated. The grafts themselves become soluble in water if each monomer unit is sulfonated. If a chain scission occurs, due to e.g. a radical attack, the polymer chain will 'flush' out with during FC operation, whereas a polymer chain with inert spacers may not be as prone to flush out.
New chemical moieties for proton conduction (at elevated temperatures) such as the triazole or tetrazole moiety and/or their ionic liquid pendants are very interesting candidates for new polymer membranes that may be synthesised.
Synthesis that avoids the harsh and environmentally unfavourable sulfonation process should be investigated. The nitroxide mediated radical polymerisation process (a controlled radical polymerisation) actually allow for the polymerisation of sulfonated monomers or other proton conducting monomers thus alleviating the sulfonation step. However, this 'breaks' with the idea of working with a preformed film.

3 Physical properties

3.1 Conductivity

The conductivity has been measured on two sets of grafted membrane samples: Both the PVdF and ETFE samples are grafted with either styrene or methylstyrene, however only ETFE has been copolymerised with different amounts of divinylbenzene (DVB) as cross-linker.
Before measurements the samples were equilibrated with water at 90 ^{o}C for one hour and subsequently cooled to room temperature. The membranes were then transferred to the measuring cell, see appendix C.
Two conductivity measuring methods were used:

1. Four point dc conductivity.
2. Impedance spectroscopy.

In the four point dc method a strip of the membrane is placed between two current electrodes. Between the current electrodes point shaped potential (sensing) electrodes are placed. By passing a known current through the samples and measuring the potential drop between the potential sensing electrodes the ohmic resistance of the sample can be calculated using ohms law. The advantage of the method is that it is simple and the contribution from the electrode reaction to the ohmic resistance is eliminated. The disadvantage is that it can only measure the conductivity in plane with the membrane, not across the membrane. It cannot be used to characterize membranes with added electrodes either. The method, however, have proven to be reliable and give consistent results. The conductivity of Nafion® (fully wetted) always corresponds to literature values.
By the impedance method the conductivity is determined for the membrane and electrodes at different frequencies, typically in the range from 1 MHz - 100 kHz to 0.1 Hz[45,46,47]. As the time constants for the electrode processes and the membrane conductivity are different, the individual contributions can be separated. The method may be used to measure in plane as well as cross plane conductivities. In the present work an electrochemical work station from Zahner Elektronik or BioLogic Instruments was used. The method is currently being established and hence results have been of varying quality. Determination of conductivity by impedance measurement, however, can be both faster and automated and since it measures the conductivity across the membrane the method will be established as the reference method.
The conductivity for the two methods can be calculated by:
Four point dc:

Resistivity (specific resistance)
$$R = \rho \cdot \frac{l}{A} \qquad 6)$$

Ohm's law
$$U = R \cdot I \qquad 7)$$

Combining 6) and 7) yields
$$\kappa = \frac{1}{\rho} = \frac{I \cdot l}{U \cdot A} \qquad 8)$$

where
κ: specific conductivity, $AV^{-1}cm^{-1}$ ($\Omega^{-1}\cdot cm^{-1}$ or $S\cdot cm^{-1}$)
I: current, A
l: length, cm
U: voltage, V
A: cross sectional area, cm^2.

Impedance:

The membrane resistance (R) is obtained from the intercept of the impedance curve, see figure 3.1.1, with the real-axis at the high-frequency end. In order to find the intercept with the real-axis the spectrum is extrapolated with a circle. The proton conductivity of membrane is calculated according to 9)

$$\kappa = \frac{l}{R \cdot A} \qquad 9)$$

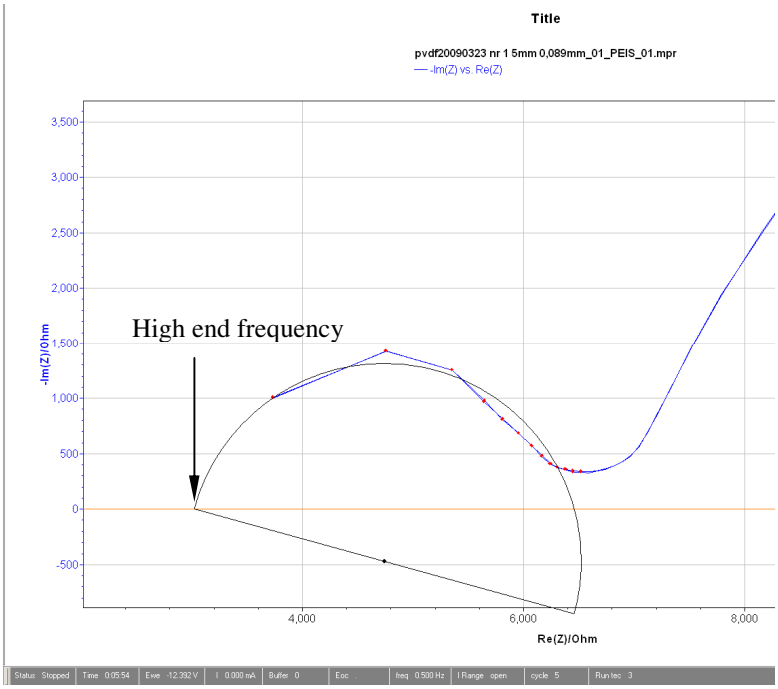


Figure 3.1.1 Impedance spectrum of a membrane. The intercept between the high end and the real-axis is extrapolated via a circular fit to the spectrum.

Measured conductivities for both cross-linked and non-cross-linked membranes can be seen in table 4.1.1. Although the conductivities measured with the impedance method is in the same order of magnitude as the DC measurements it still require optimisation before it can substitute this.

As can be seen membrane materials with conductivities with almost twice the conductivity of Nafion® has been prepared in the project.

Batch	X-linked	DC conductivity S/cm	Impedance S/cm
Nafion®	-	0.090	0.170
ETFE			
ETFE-2007-06-11-1	+	0.007	
ETFE-2007-07-02-1	+	0.001	
ETFE-2007-10-23-3	+	0.075	0.025
ETFE-2008-02-25-1	+	0.022	
ETFE-2008-09-17-1	+	0.003	
ETFE-2008-09-22-1	+	0.027	
ETFE-2008-09-22-2	+	0.031	0.093
ETFE-2008-09-29-1	+	0.006	
ETFE-2009-04-22-4	-	0.027	0.027
ETFE-2009-04-28-4	-	0.062	0.025
PVdF			

Batch	X-linked	DC conductivity S/cm	Impedance S/cm
PVDF-2008-02-04-1	+	0.045	
PVDF-2009-01-20-2	-	0.079	
PVDF-2009-01-20-4	-	0.095	
PVDF-2009-03-04-2	-	0.092	0.013
PVDF-2009-03-04-3	-	0.053	0.013
PVDF-2009-03-18-5	-	0.124	0.015
PVDF-2009-03-18-6	-	0.125	0.011
PVDF-2009-03-19-2	-	0.099	0.139
PVDF-2009-03-19-4	-	0.093	0.105
PVDF-2009-03-23-2	-	0.091	0.151
PVDF-2009-03-24-4	-	0.149	0.017
PVDF-2009-03-25-1	-	0.147	0.025
PVDF-2009-03-25-2	-	0.119	0.018
PVDF-2009-04-22-3	-	0.097	0.029
PVDF-2009-04-28-3	-	0.055	0.013

Table 3.1.1 Conductivities of selected membranes measured with 2 different techniques. Impedance measurements still require optimisation.

As mentioned in the previous section cross-linking does affect the conductivities. In the work of M.J. Larsen[27] (in the context of this project) the conductivity was investigated as a function of cross-linker concentration, see figure 3.1.2. In the figure the results form the cross-linked membranes are shown together with the conductivity of Nafion® under similar conditions. The cross-linker concentration will affect the conductivity, however, conductivities in the same order of magnitude as Nafion® can be achieved.

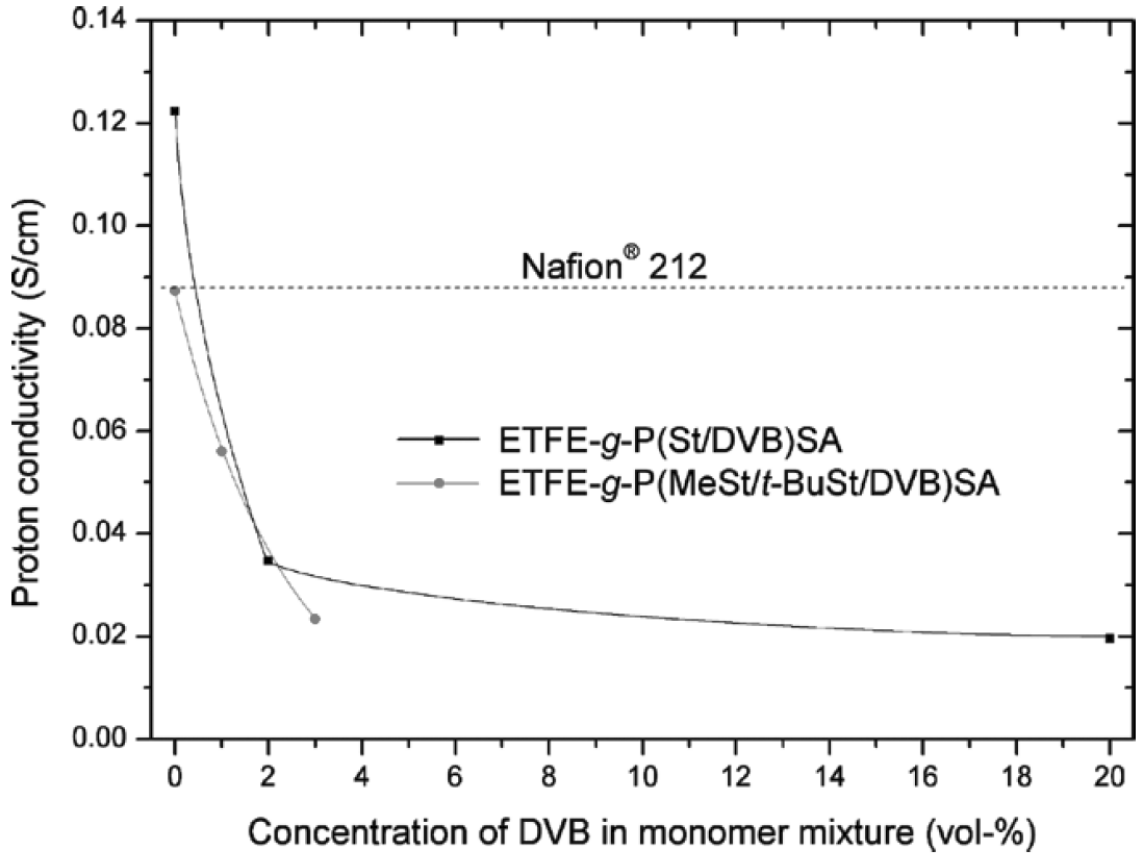


Figure 3.1.2 Conductivity as a fct of cross-linker level for various types of membranes.

Different sulfonating methods[27] were also tried, namely sulfonation via trimethylsilyl chlorosulfonate or acetyl sulphate complexes, in order to circumvent the detrimental effects of the harsh direct sulfonation via chlorosulfonic acid. However, direct sulfonation proved the most efficient method. In the course of the grafting process the polymer growth is random in the sense that the growing polymer segments are not oriented in any direction. The segments however are locked with respect to each other due to the grafting matrix. When sulfonating the segments this sulfonation is also random in terms of orientation – more important, however, is that the sulfonated segments are still 'locked'. The use of cross-linker when grafting prohibits the dissolution and reorientation of the segments. As can be seen from table 4.1.2 the average molecular weight per sulfonate group (derived from IEC-values) of the grafted samples indicate that low average molecular weights per sulfonate group compared to Nafion® have been achieved. Although the aromatic sulfonate moiety does not possess the same acidity as the perfluorosulfonate moiety this low average molecular weight ought to have translated into a better conductivity! If the sulfonated segments are allowed to reorient themselves during a dissolution/recasting process better conductivities ought to be attainable – and at the same time (as mentioned in previous sections) achieve better tensile properties for the membrane.

Batch	**IEC (meq/g)**	**Av. Mol weight pr. Sulfonate group**	**Monomers**
Nafion®	0.9	1100	
ETFE			
ETFE-2009-04-28-2	2.06	485	MTY
ETFE-2009-04-28-4	2.09	478	MTY
PVdF			
PVDF-2009-03-04-2	1.67	599	MAN
PVDF-2009-03-04-3	1.50	667	MAN
PVDF-2009-03-19-1	1.79	559	MTY/MAN
PVDF-2009-03-19-3	1.81	552	MTY/MAN
PVDF-2009-03-23-1	1.77	565	MTY/MAN
PVDF-2009-03-23-3	1.89	529	MTY/MAN
PVDF-2009-03-24-1	2.22	450	MTY
PVDF-2009-03-24-2	2.23	448	MTY
PVDF-2009-03-24-3	2.11	474	MTY
PVDF-2009-03-24-4	2.18	459	MTY
PVDF-2009-03-25-1	2.22	450	MTY
PVDF-2009-03-25-3	2.24	446	MTY
PVDF-2009-04-28-1	1.60	625	MTY
PVDF-2009-04-28-3	1.32	758	MTY

Table 3.1.2 IEC-values and the corresponding average molecular weight per sulfonate group for the membrane.

Thus it was decided to graft only the main constituents either methylstyrene, methylstyrene/methacrylonitrile (and methacrylonitrile) without the cross-linker. The work with this approach unfortunately could not be finished in this project, but will be continued in another project.

3.2 Solvent uptakes

Water uptake

Water uptake has been determined as function of temperature and relative humidity for a series of PVdF-g-PSSA and ETFE-g-PSSA membranes

The properties of the selected membrane samples are shown in the table 3.2.1

Batch	DOG (mass%)	DOS (mass%)	Water content @ RT (mass%)
PVdF 2009-01-20 -4	131.38	53.29	99
ETFE 2008-09-22-1	53.65	NA	24
ETFE 2008-09-22-2	58.82	NA	18

Table 3.2.1 IEC-values and the corresponding average molecular weight per sulfonate group for the membrane.

The membranes were boiled in distilled water and kept in contact with liquid water until use. To determine the total water content the samples were wiped dry with tissue paper and then dried at 80 °C in a vacuum oven connected to a liquid nitrogen trap[48].

It was examined whether the Schröeder's paradox[49,50] – the fact that the solvent content is different for membranes equilibrated in contact with liquid water is markedly different from the water content for membranes equilibrated with water vapour in equilibrium with liquid water - applied for these membranes. It turned out not to be the case.

To determine the water content at different temperatures and relative humidities a clima cabinet was used (Memmert HCP 108). The temperature can be programmed in the range form 5 degrees above ambient to 90 °C and the relative humidity can be programmed as well. The weigth of the membranes were determined at 22 °C (room temperature) as well as at 40, 60 and 80 °C and at 30, 50, 70 and 90 % relative humidities.

The results are shown in the figure 3.2.1

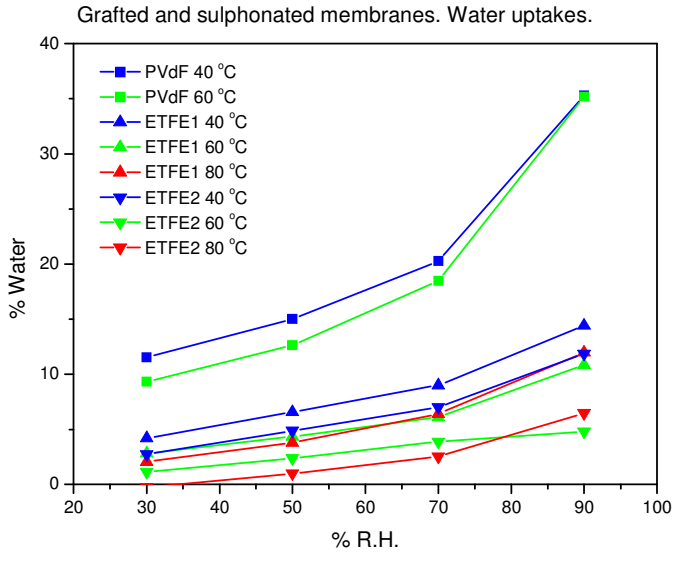


Figure 3.2.1 Water uptake as function of relative humidity for selected membranes.

As can be seen all membranes and in particular PVdF loose water when the relative humidity is lowered and/or the temperature increased. At 80 °C the PVdF membrane become so sticky that continued measurements were impossible. Cross-linked membranes do not absorb as much water as non-cross-linked membranes, however, they do not lose water as fast when the RH is lowered.

The water content in cross-linked equilibrated membranes is generally low. The physical orientation of the sulfonated polymer segments is not optimal.

Water and methanol uptake

The work on water and methanol uptake has been conducted by Y. Ma[48] with membranes prepared in the project, PSO no.: 4073**.** The properties of the membrane samples are listed in the table 3.2.2. It should be noted that polymer matrix used for grafting was ETFE, 50µm, and the membranes were grafted with styrene and sulfonated with chlorosulfonic acid.

	DOG (mass%)	DOS (mass%)	Dry Mass (g)
FS 7-1	49.80	95.34	0.4927
FS 7-2	35.17	101.97	0.4313
FS 7-3	61.86	99.72	0.4851
FS 7-4	57.90	96.49	0.4795
FS 8-5	71.81	44.22	0.4102
FS 8-7	12.72	99.17	0.3055

Table 3.2.2 Properties of membranes prepared in project PSO no. 4073.

The membranes were boiled in 1M sulphuric acid and distilled water, 1 hour for each step. After the pre treatment, the samples were dried in vacuum (~0.1 mbar) at 80°C for 30 mins. The membranes were equilibrated at room temperature for 20 hours in a large excess (~500 ml) of different water-methanol mixtures covering the range from pure water to pure methanol. After equilibration, the samples were dried in vacuum (~0.1 mbar) at 80°C for 30 mins.

To recover the dry membranes, they were reboiled in distilled water for 1 hour. All the samples were employed repeatedly for 10 times, and stored in distilled water.

The solvent uptake is defined as the mass of absorbent liquid divided by the mass of dry membrane.

The data of total solvent uptake in ETFE-g-PSSA membranes are plotted in figure 3.2.2 along with the data of total solvent uptake in Nafion® 117 membrane.

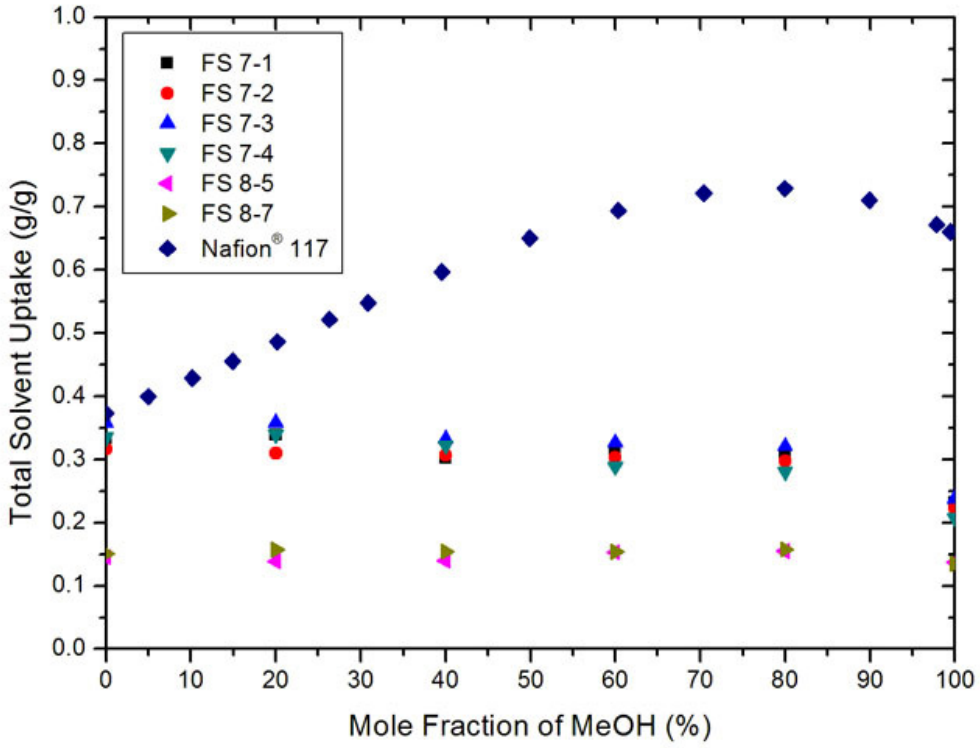


Figure 3.2.2 Water and methanol uptake as a function of the methanol mole fraction.

The total solvent uptake characteristics of water-methanol mixtures in ETFE-g-PSSA and Nafion® 117 membranes are evidently different. In the case of Nafion® 117 membrane, the total solvent uptake increases as the methanol concentration increases. When a methanol mole fraction of ~80% is reached, the total solvent uptake passes through a maximum value. Then the total solvent uptake decreases as the methanol concentration gets higher. In the case of each ETFE-g-PSSA membrane, the total solvent uptake decreases gradually as the methanol concentration increases, over the whole range.
The data of individual solvent uptake in ETFE-g-PSSA membranes are plotted in figure 3.2.3.

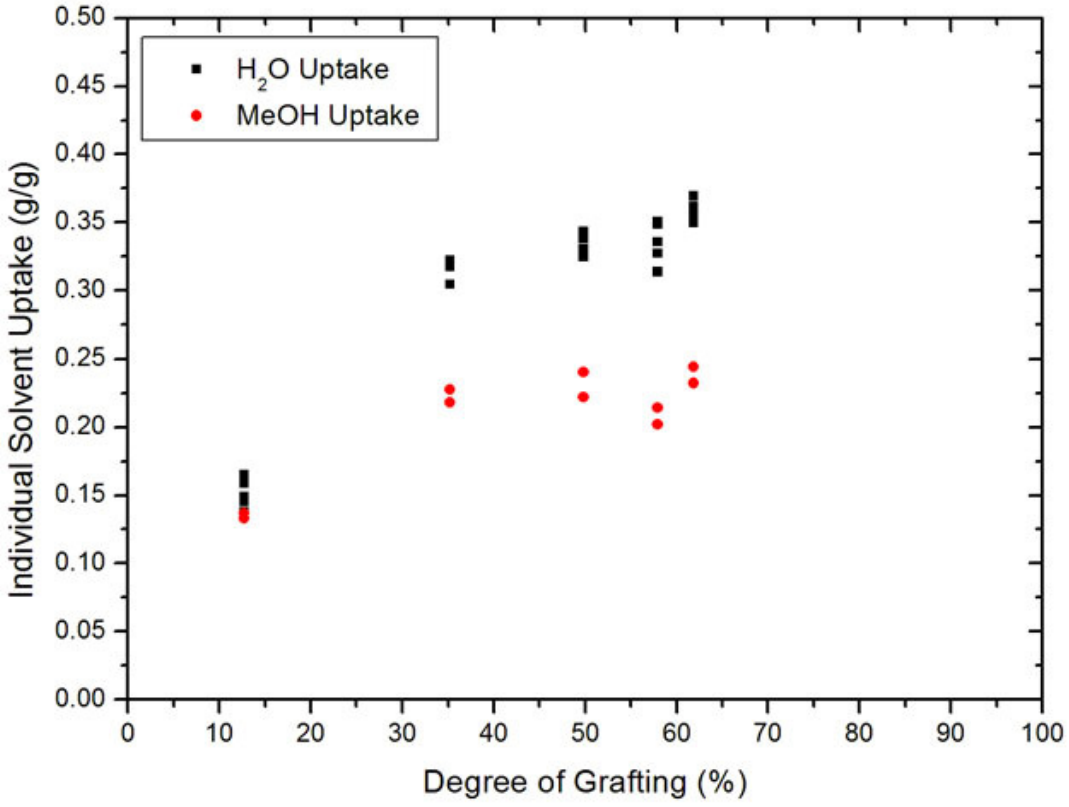


Figure 3.2.3 Water and methanol uptake as a function of DOG.

The individual solvent uptake in ETFE-g-PSSA membranes shows an increasing trend at a given range of DOG. However, sample FS 8-5 is not included, which is mainly due to a low DOS. The water uptake varies from 0.1512 g/g to 0.3599 g/g, and approaches the value of 0.3726 g/g for Nafion® 117 membrane at the highest DOG. The methanol uptake varies from 0.1349 g/g to 0.2381 g/g, and differs much from the value of 0.6688 g/g for Nafion® 117 membrane at the highest DOG.
The mechanical property of ETFE-g-PSSA membranes becomes insufficient at high DOG – it is very brittle. Furthermore, each membrane experiences a gradual loss of weight. These factors may impose uncertainties in the determination of solvent uptake.
As can be seen from the plots the ETFE-g-PSSA membranes are found to have preferential uptake of water from water-methanol mixtures. This may indicate that this type of materials will show a reduced methanol cross over compared to Nafion®.

3.3 Stability studies

Two types of *ex-situ* stability studies have been performed.

1. Chemical stability. In addition lifetime – defined as the time for loss of 10% of the initial weight when treated with a 3% solution of hydrogen peroxide – has been determined for a series of grafted and cross linked membranes (cross-linked with divinylbenzene, DVB, and with methylstyrene, MTY). This test is often referred to as "Fenton's test".
2. Thermal and chemical stability. The chemical and thermal stabilities of the PVdF-2009-01-20-4, ETFE-2008-09-22-1 and ETFE-2008-09-22-2 membranes was studied by treatment with 20% hydrogen peroxide at 80 °C and by thermogravimetry combined with mass spectrometry.

Chemical stability

The treatment with hydrogen peroxide is believed to mimic the conditions at the electrodes[51] where radicals may be formed during the electrochemical reduction of oxygen and by the formation of water by the chemical reaction of hydrogen and oxygen caused by gross over of the gases, see figure 3.3.1[52].

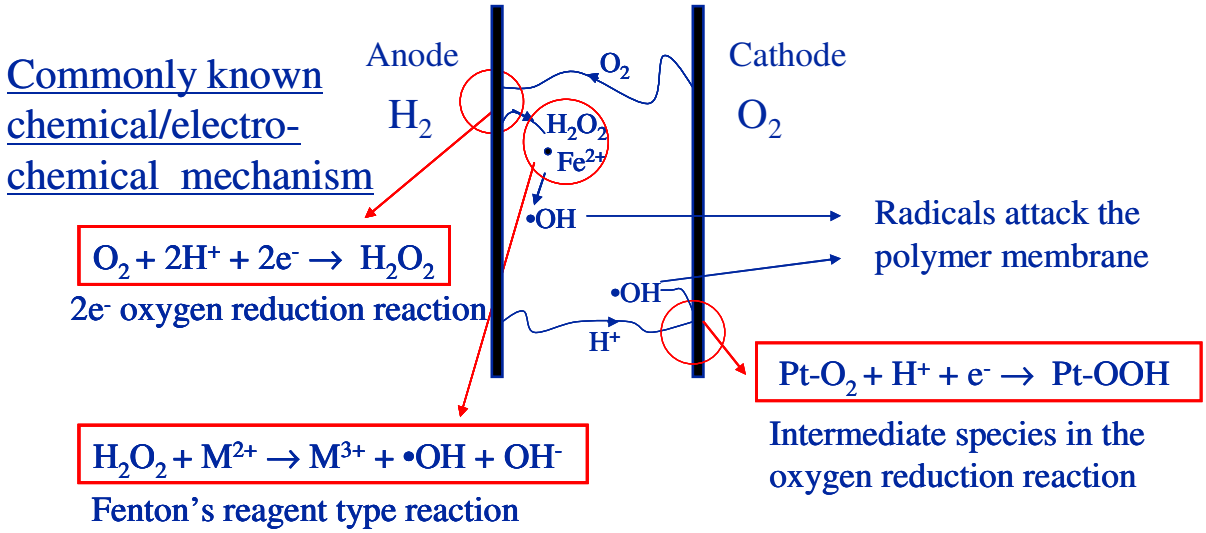
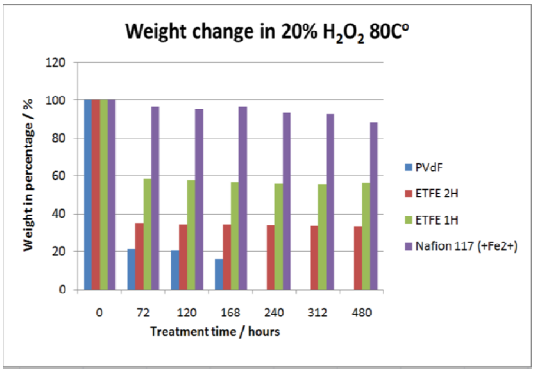


Figure 3.3.1 Proposed mechanisms for the formation of radicals within the membrane and electrodes[52].

The weigth loss was followed as function of time and the results are shown in the figure 3.3.2 below. For comparison also results obtained on Nafion® are shown.
It is evident that membranes without cross-linking (PVdF) does not provide adequate durability in this ex-situ test. The cross-linked ETFE membranes appear to be better, however, the weight loss is very likely for associated with the graft and not the matrix polymer and hence it may be concluded that they are only marginally better than the PVdF-sample. Although the Fenton's test gives an indication of radical stability it is only qualitative. It is not possible to correlate the results to actual FC performance[52] and membrane stability cannot be deduced from Fenton's test. The proposed degradation mechanisms are not entirely consistent and were primarily based on *ex-situ* fuel cell tests[52].



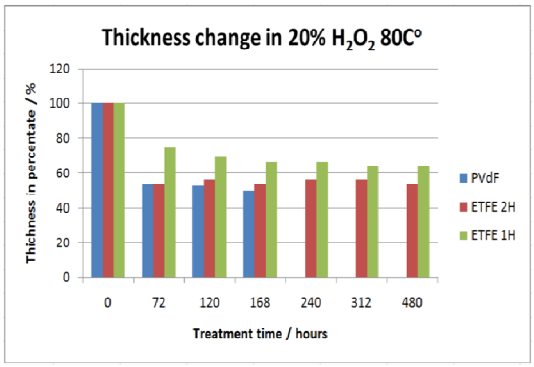


Figure 3.3.2 Weight and thickness loss as a function of time for

Membranes grafted with styrene or methylstyrene and cross linked with divinylbenzene

In the figure 4.3.3 below the lifetimes as function of the degree of cross linking is shown

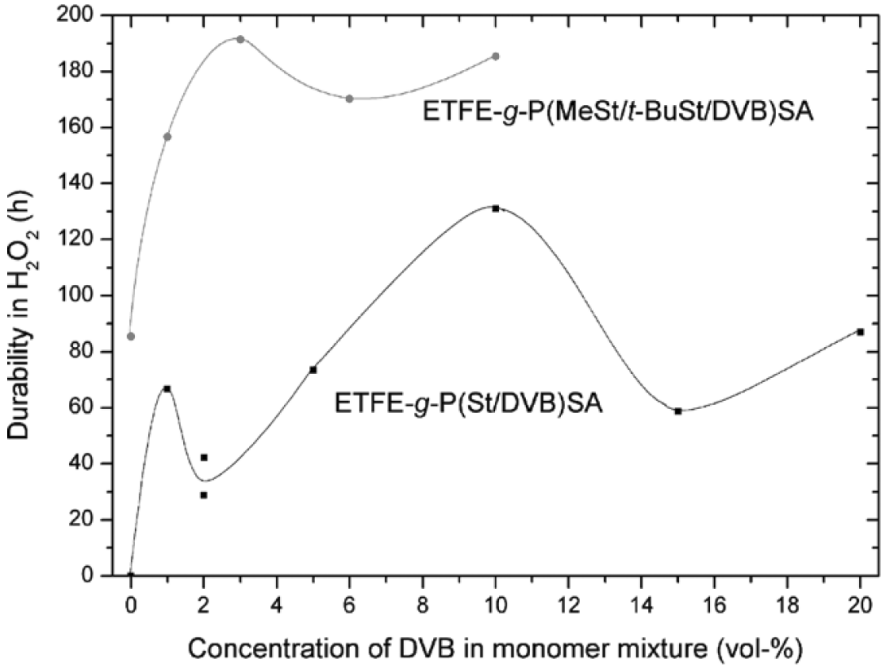


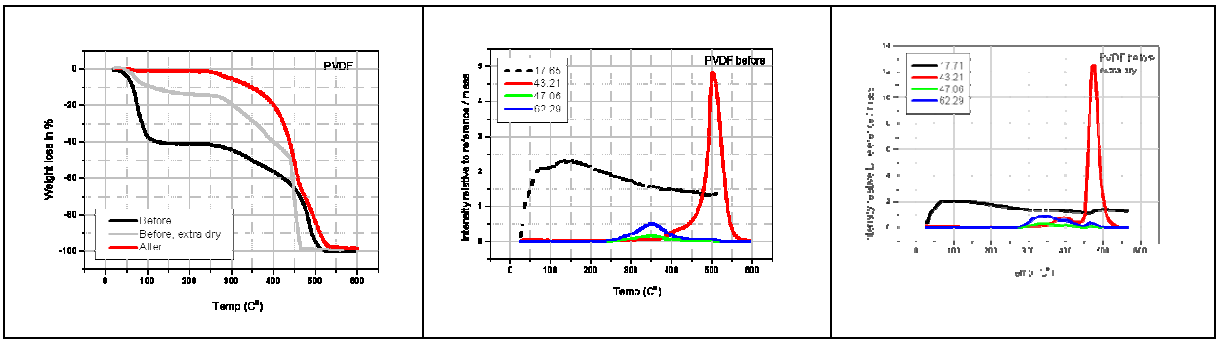
Figure 3.3.3. Membrane stability (Fenton's test) as a function of cross-linker content.

It is evident that grafting with methylstyrene and/or methylstyrene and tert-butylstyrene produce more stable membranes.

Arkema[53] is producing a blended PVdF membrane with a proprietary polyelectrolyte. This membrane shows good chemical resistance in the ex-situ test.

Thermal stability

Samples of the membranes taken before and after the treatment with hydrogen peroxide was placed in a themobalance (Setaram tg98) and heated slowly to 600 °C in argon containing 20% oxygen. The outlet gas was led to the membrane inlet of a mass spectrometer (Varian MAT) thus allowing the composition and thereby the degradation products to be determined. This was done by following the intensities of mass 18 (water), 44 (CO_2), 48, 63, 68 (fluorine containing fragments) and 64 (SO_2). The results are shown in figure 3.3.4 below:



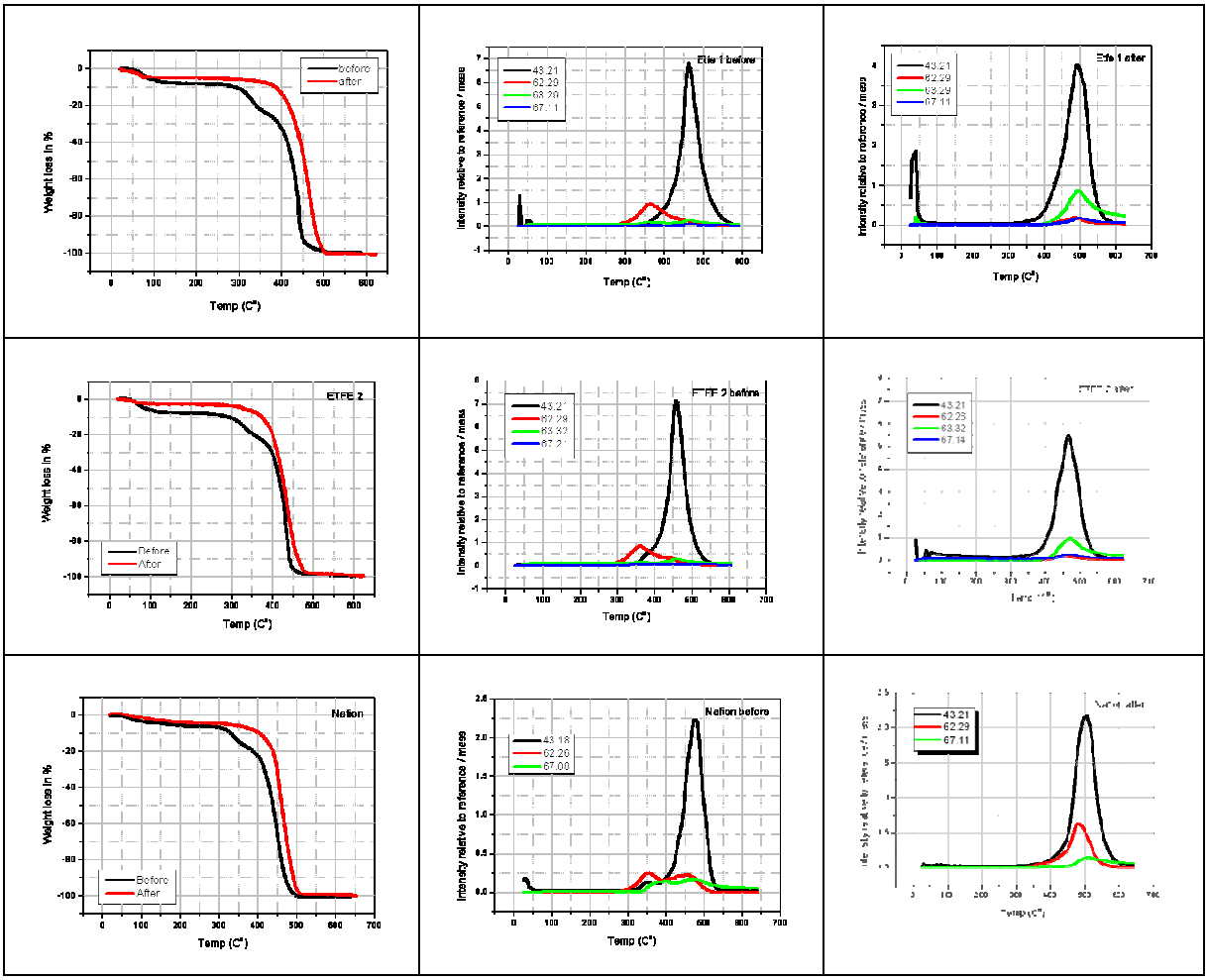


Figure 3.3.3 TG/MS spectra of membranes heated to 600°C. The black curve is the pristine membrane and the red curve is the membrane exposed to Fenton's test. The gaseous products were monitered by mass spectrometry. The degradation products could be determined by following the intensities of mass 18 (water), 44 (CO_2), 48, 63, 68 (fluorine containing fragments) and 64 (SO_2).

For all the membranes a water loss is observed at temperatures around 100 °C. For the ETFE and Nafion membranes the weigth loss around 350 °C for the untreated membranes caused by sulphur containing groups is missing for the treated membranes (the red curve is missing). This means that the radical attack from hydrogen peroxide causes loss of sulphonic acid groups. A similar behavior is seen for PVdF, but for this material also fluorine containing groups are lost at 350 °C. Comparison with the weigth loss curves shows that the degradation of Nafion is significant lower that for the grafted membranes, but the degradation patterns are found to be similar.
Further characterisation of the membranes have been conducted in the project PSO 2007-1-7156.

3.4 Student projects

During the project three master students has been associated to the project by doing their master thesis project within the projects topics.
The three students are:
Mikkel Juul Larsen worked on grafting and cross linking of EFTE based membranes. This work resulted in membranes based on a mixture of methyl styrene, tert-butyl styrene and divinyl benzene and the promising results were continued in the present project. The work of

Mikkel Juul Larsen is reported elsewhere in this report[27] and has also been presented/published at conferences and in articles.54
Pelle Funder Michelsen and Morten Skovsen worked on "Composite Polymer Electrolytes" in a joint project. See below in 3.4.1.

3.4.1 Composite polymer electrolytes

The background for the project was the discovery in the group of materials chemistry at SDU around 1990 that inorganic protonic conductors could be synthesized by trapping nano particles of hydrous tinoxide in the cavities of acid resistant zeolites - in particular the zeolite mordenite - [1]. The zeolite material is composed of micrometer sized particles so a binder system is needed in order to prepare membranes. Due to its inorganic nature the material was expected to have a much reduced methanol cross over compared to pure organic materials and a composite electrolyte for DMFC use consisting of the zeolite mixed with a suitable binder was envisaged.
Problems arose when synthesis was attempted transferred from laboratory scale to pilot plant scale. The reason was suspected to be due to change of zeolite supplier, but analytical tools was not available to the materials chemistry group at that time to pursue the problem and promising polymer membranes had arrived.
In the meantime in particular solid state Al-NMR and SEM-EDX equipment has been available to the group on site and it was decided to reinvest the materials
As binder Nafion® was chosen as it can easily be dissolved and reprecipitaded from alcohol-water mixtures and the project partners was experienced in using the material as binder in electrodes.
Zeolites are aluminosilicates where aluminium is replacing silicon in a tetraedrical coordinated silicon-oxygen framework. For each aluminium in the framework a positive ion must be housed in the zeolite cavities in order to preserve charge neutrality. This property makes the materials inorganic ion exchangers and is the background for the use of zeolites in washing powders. The positive ion may be a proton, but then the material becomes an acid and only a few zeolites are stable under acidic conditions - among them the zeolite Mordenite used in the present work. During acid attack aluminium in the framework is released and will then exist as positive hydrous (polymeric) aluminium ions in the zeolite cavities. These aluminium ions may be expected to influence the ion exchange properties and thereby the possibility to introduce other metal ions with possible proton releasing properties. The extra framework aluminium is, however, in an octahedral coordination and can be differentiated from the tetradrically coordinated aluminium in the framework by Solid State Al-NMR.
The base material, H-Mordenite (Zeolon-100H from Norton Chemical Process) was found to contain approx. 17% octahedral aluminium as an impurity. Treatment with acids as nitric acid, oxalic acid or acetic acid did not remove the impurity while treatment with aqueous NaOH (0.5 M) did. The mordenite was in the later cleaning process converted into the sodium form (Na-mordenite) and had to be converted back to the hydrogen form. Treatment with different acids including weak organic acids and ammonium nitrate solutions unfortunately recreated a content of octahedral aluminium similar to the base material.
In the preparation of the tinoxide containing mordenite (tin-mordenite) tin(II) ions are ion exchanged into the mordenite structure by treatment with molten $Sn(II)Cl_2,2H_2O$ followed by an oxidation with oxygen (in air) at 400 ^oC. In this step nanosized particles of tin(IV) oxide is formed. By subsequent washing with water the particles are hydrated at the surface forming a surface layer of tin(IV) acid which is a good protonic conductor.
As the purification experiments showed that octahedral aluminium may be removed by ion exchange it was decided to treat the base material as well as the Na-mordenite by the tin-mordenite procedure. When the molar ration of $SnCl_2$ to mordenite was below one the low

content of octahedral aluminium in the Na-mordenite was preserved. For all other preparations an octahedral aluminium content comparable to the base material was found.
In order to optimize the binder content the interaction between Nafion® and the zeolite material was studied by adsorption measurements. Known amounts of zeolite was dispersed in Nafion® solutions by ultrasonic treatment. The concentration of Nafion® in the solution before and after the treatment was determined by ^{19}F-NMR. From the measurements the relation between the concentration of free Nafion® in the solution and the amount adsorbed at the surface of the zeolite (the adsorption isotherm) could be calculated. In contrast to the behavior of the carbon substrates used for electrode preparation Nafion® was not found to adsorb on the zeolites in any appreciable amount.
In spite of the above findings composite tin-mordenite- Nafion® membrane samples were made by mixing zeolite and Nafion® solution in a ratio giving 30 Wt% Nafion® in the samples after drying. Samples of 1 mm thichness and a diameter of 1 cm were prepared by compaction in a hydraulic press. EDX measurements on cross sections showed the Nafion® to be evenly distributed. The samples were equipped with indium electrodes and the conductivity measured by impedance spectrometry. In contrast to earlier findings[55] where conductivities in the order of 10^{-2} ohm^{-1}cm^{-1} were found the samples were found to have very low conductivities in the order of 10^{-9} ohm^{-1}cm^{-1} for samples without Nafion® binder to 10^{-6} ohm^{-1}cm^{-1} for samples with binder. The reason for the low conductivities is not clear, but layering in the samples used for the conductivity measurements was observed and may have given rise to bad contact throughout the sample.

Tin oxide Nafion® composites

Water containing Nafion® in the form of membrane material is a self assembled structure consisting of nano sized water filled cavities connected by channels embedded into a perfluorinated hydrocarbon framework. Sulphonic groups protruding into the cavities and channels gives rise to the high protonic conductivity (in the order of 10^{-2} ohm^{-1}cm^{-1}) and do also give rise to an ion exchange capacity. It was therefore attempted to introduce the tin oxide nano particles into the Nafion® structure using the method developed for the zeolite materials.
The ion exchange was done with tin(II)chloride dissolved in methanol on acid treated Nafion® samples (H-form) dried at 80 ^{o}C in vacuum. Tin(II)chloride solutions ranging from 0.25M to 2.00 M were used and the exchange time was set to 24 hours. After ion exchange the solvent was removed by heating to 80 ^{o}C in for 2 hours and the materials were subsequently oxidized by oxygen in air at 80 ^{o}C followed by boiling in 3% hydrogen peroxide solution. Even distribution of tin throughout the samples was confirmed by EDX element mapping and the conductivity was determined using impedance spectroscopy on samples squeezed between Nafion® membrane samples equipped with standard fuel cell Pt electrodes kept at 96 % R.H.
The tin content in the samples increased with increasing tin concentration in the methanol solution. In contrast the water content in the humidified samples and the conductivity decreased with increasing tin content. The water content at room temperature dropped from 25 % for pure Nafion® to 19 % for the sample with the highest tin content. The tin to sulphur (sulphonic acid groups) ratio showed that tin in excess of the ion exchange capacity was introduced into the Nafion® structure. The protonic conductivity at room temperature was found to decrease from $6.5\text{x}10^{-2}$ ohm^{-1}cm^{-1} for pure Nafion® to $8.7\text{x}10^{-3}$ ohm^{-1}cm^{-1} for the sample with the highest content of tin. Time did not allow determination of mechanical properties, methanol cross over measurements or fuel cell tests, but the materials are found to be so promising that the work will be continued.

3.5 Concluding remarks on physical characterisation

Unfortunately the membranes from DTU did not have sufficient conductivity to conduct an extensive characterisation, however, some of the results were very promising and research in these membranes will continue.

The radiation grafted membranes do show good conductivities, which is a prerequisite for proper fuel cell performance and conductivities that surpass that of Nafion® can easily be obtained. Conductivities 1.5 times that of Nafion® have been obtained. Adding a cross linker to the membrane improves the chemical stability and it appears that choice of matrix (PVdF vs. ETFE) may also have a little influence on the stability, however this has not been investtigated thoroughly. Adding cross linker also reduces the conductivity and increases the brittleness, however, as Arkema[53] has shown, good stable membranes with a blended membrane (matrix) may be obtained and initial studies with the use of a matrix are promising and studies in this will be continued.

4. Fuel Cell testing

4.1 Commercial membranes.

Initially the market for alternative commercial membranes were searched.
Several commercial suppliers of membranes were identified. Most of these membrane suppliers only supplied fluorinated membranes, see table 4.1.1. However extensive R&D in alternative membranes have been conducted, both partially fluorinated and non-fluorinated (hydrocarbon), and the type and producer of these are also indicated in table 4.1.1. The colour in the tables indicate the type of FC testing, which has been conducted with the membranes.

Producer	Trade name/ Abbreviation	Comment
Producers of commercial perfluorinated PEM (fully fluorinated)		
Du Pont	Nafion®	Long side chain. Structure, see table 5.2 Du Pont has been developing a Nafion® with better stability. Nafion® CS Efficient operation only up to 80°C[56]
Solvay Solexis	Hyflon Ion	Short side chain. Lower EW. Larger temperature operation window. More crystalline (than Nafion®) [57]
3M	?	Short side chain. Structure, see table 5.2. Only sold commercially as a Membrane Electrode Assembly, MEA.
Asahi Chemical Company	Aciplex S	Structure, see table 5.2.
Asahi Glass	Flemion	Structure, see table 5.2 (like Nafion®) Have developed a PEM for continuous operation at 120°C[58]
Golden Energy Fuel Cell (GEFC)	GEFC	Structure unknown. Efficient operation only up to 95°C
Gore	Gore Select	Teflon impregnated with Nafion® [59]
(Lydall) Solutech	?	UHMWPE impregnated with Nafion®.
Fumatech	Fumion F	Structure unknown. Efficient operation up to 95°C [60]
Dow	Dow XUS	Short side chain. Not produced anymore. Same as Hyflon Ion.
Partially fluorinated PEM		
Arkema	KYNAR® PVdF	Blended copolymer (formerly polyAMPS) [61]. Not yet commercially available.
Paul Scherrer Institute	FEP ETFE	Monomers: Styrene and α-methylstyrene [62]. Only R&D products.
IRD/SDU	FEP ETFE PVdF	Monomers: Styrene [63] and substitued styrenes. Only R&D products.
University of Pavia	PVdF PVdF-co-HFP	Monomers: Styrene [64].
Japan Atomic Energy Research Institute	ETFE	Monomers: methylstyrene, tert-butylstyrene 65.
Naval Materials Research Laboratory (India)	FEP	Monomer: Acrylic acid (converted to sulfonic acid) [28, 66].
Ballard	α,β,β-trifluorostyrene	BAM3G, produced by radical polymerization from its constituent monomers.
CEC, Japan	ETFE	RAYMION, commercially available for separation processes[29]. α,β,β-trifluorostyrene used as grafting monomer.
RAI, USA	PTFE	PERMION, commercially available for separation processes [29]. Styrene used as grafting monomer.
Developers of PEM with a hydrocarbon backbone.		
General Electric	S-PS	Monomer: Styrene. The PEM was used in the Gemini program.
DAIS Analytic	S-SEBS	Monomers: Styrene, ethylene and butylene. SEBS systems are known block copolymers, e.g.

Producer	Trade name/ Abbreviation	Comment
		Kraton G 1650[59]. Probably sulfonated using the sulfur trioxide/triethyl phosphate method.
Pirelli Labs	PE-g-PSSA	Monomers: Ethylene grafted with styrene. Grafted with polystyrene, PS [67].
Gwangju Institute of Science and Technology, Korea	S-(PS-b-poly(Et-r-Bu)-PS)	Monomers: Styrene, ethylene and butylene. Block copolymer that phase separates. Sulfonated using the acetyl sulphate method [68].
University of Newcastle upon Tyne, Cranfield University	LDPE-g-PSSA	Monomers: Ethylene grafted with styrene. Grafted with polystyrene, PS. Postsulfonated with chlorosulfonic acid[69].
Polyfuel	?	Stability issues would probably reveal the nature of the backbone e.g. aromatic or aliphatic. Results are confidential.
Hoku Scientific	poly(4-phenoxybenzoyl-1,4-phenylene) (sPPBP)	Hoku Scientific has cooperated with Nissan to develop the membrane.

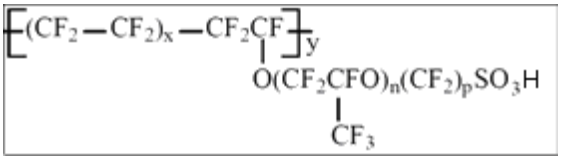
Table 4.1.1 Companies/groups who has been developing PEMs with ahydrocarbon backbone.

Standard, reference membrane. Extensive FC testing.

Tested in standard size IRD MEA.

Tested in small size MEA.

Tested in other projects at IRD.



Du Pont	Solvay Solexis	Asahi Glass	Asahi Chem. Com.	3M,
Nafion® [70]	Hyflon Ion [70]	Flemion T [70]	Aciplex S [70]	Name: ?
EW: 1100, 1200	EW: 790, 830, 870	EW: 1000	EW: 1000 - 1200	EW: ?
x: 5-13	x: 3.5 - 10	x: 5 - 13	x: 1.5 - 14	x: ?
n: 1	n: 0	n: 0 - 1	n: 0 - 1	n: 0
p: 2	p: 2	p: 1 – 5	p: 1 – 5	p: 4 [71]

Table 4.1.2 Identification of structural components and monomers in commercial perfluorinated ionomers.

In general the market is mostly dominated by perfluorinated membranes as these (up until recently) has shown superior durability compared to membranes only partially fluorinated or with a hydrocarbon backbone. The research in membranes with non- or partially fluorinated backbones is intense and a few non-fluorinated membranes have emerged with reasonable durability. Polyfuel and Hoku Scientific are examples of companies producing non-fluorinted membranes. They are, however, quite restrictive in allowing testing of their materials.

4.2 Test of commercial membranes.

Solvay Solexis, Golden Energy Fuel Cell and Solutech have supplied membranes. Hyflon® Ion 870 (Solvay Solexis), GEFC 11-N (Golden Energy Fuel Cell) and Solupor E-40C01B (Solutech, a subsidiary of Lydall, formerly DSM), have been tested for durability in a stack.

Suppliers of non-perfluorinated membranes have been contacted. However most companies either did not reply or did not want to supply membranes. Polyfuel eventually did supply their hydrocarbon membrane, however, only for testing with DMFC.

The two first membranes are not reinforced whereas the last is Nafion® embedded in a UHMWPE matrix. The method of synthesis often indicates the cost of production. However, the synthesis method is only outlined[70] for Hyflon (chemically similar to the Dow XUS membrane) whereas the GEFC membrane has no indication of synthesis method.
The cost of the membranes are only marginally different from the industry standard Nafion® (~ 350 US$/m^2, Nafion® 212 [primo 2009]). The reason for this similarity in cost is peculiar leading one to speculate whether other manufacturers are exploiting the possibility of increasing the revenue by closely following the cost of Nafion®.

The MEA's were prepared by standard IRD procedures, see table 4.2.1 for details. Since the MEA's have been exposed to a synthetic reformat gas the catalyst on the anode side has been an alloy of PtRu deposited on high surface area carbon black (HSA CB).

Membrane	Hyflon Ion E87	GEFC 11-N	Solupor E-40C01B
Supplier	Solvay Solexis	Golden Energy Fuel Cell	Solutech
Thickness, [µm]	30	50	30
Anode loading, [mg PtRu/cm^2]	HiSpec 10000		~ 0.3
Cathode loading, [mg Pt/cm^2]	HiSpec 9100		~ 0.5
MEA Electrode area, [cm^2]			156
Stack test conditions			
Stack load, [A]			45
Oxidant	Air	Stoich., λ_{air}= 2.7	$P_{H2O}/P_{sat\cdot 70°C}$=1.0
Fuel	H_2,75%, CO_2, 25% CO, 50 ppm Air bleed, 3%	Stoich., λ_{fuel}= 1.2	$P_{H2O}/P_{sat\cdot 74°C}$=1.0
Stack temperature, [°C]			72 – 77
Stack pressure			Ambient
Voltage degradation, [µV/h] (measured @ end of exp.)	-26.4	-11.76	-41.8

Table 4.2.1 Membrane and MEA data for the tested membranes.

All three MEAs actually performed reasonably well during their entire operational life, see figure 4.2.1 (the 'bumpy' curves is an indication of the complexity of operating a stack. The operation did give a lot of feedback with respect to Balance Of Plant [BOP]).
The test ran for 3000 hours. The only membrane to run the full duration of the test was the GEFC membrane. The other two membranes were removed to give place for other R&D membranes. One of the reasons for changing these membranes were also their more unstable behaviour – especially the FC with the Hyflon Ion membrane did show a more 'volatile' voltage.
The voltage degradation has been measured. The Hyflon and Solupor membranes showed voltage degradations that, based on where the time is 'sliced', will produce either a negative trend or a positive trend with respect to voltage degradation. A close look at figure 4.2.1 indicates that the operation of the stack improved significantly after app. 1100 hours for Solupor and 1750 hours for Hyflon (the membranes were not added simultaneously to the stack) and the actual measured degradation can be measured to anything from ~+5 to ~ -52

µV/h for the Hyflon membrane. This just illustrates how hard it is to assess the degradation and to evaluate whether a cell in a stack is ready for change, since operating conditions clearly affects the performance.
The MEAs were not post mortem analyzed for effects such as increase of ohmic resistance, membrane thinning, catalyst particle sintering, catalyst migration, support sintering, bipolar plate degradation etc.
The performance of the membranes can be characterised as satisfactory and at least as good as Nafion®. However, a lesson learned from operating the stack is that the overall durability of the membranes depends on the membrane thickness. In general thicker membranes are less prone to mechanical errors than thin membranes, Thus thicker membranes provide better durability, albeit at the expense of slightly higher ohmic resistance.

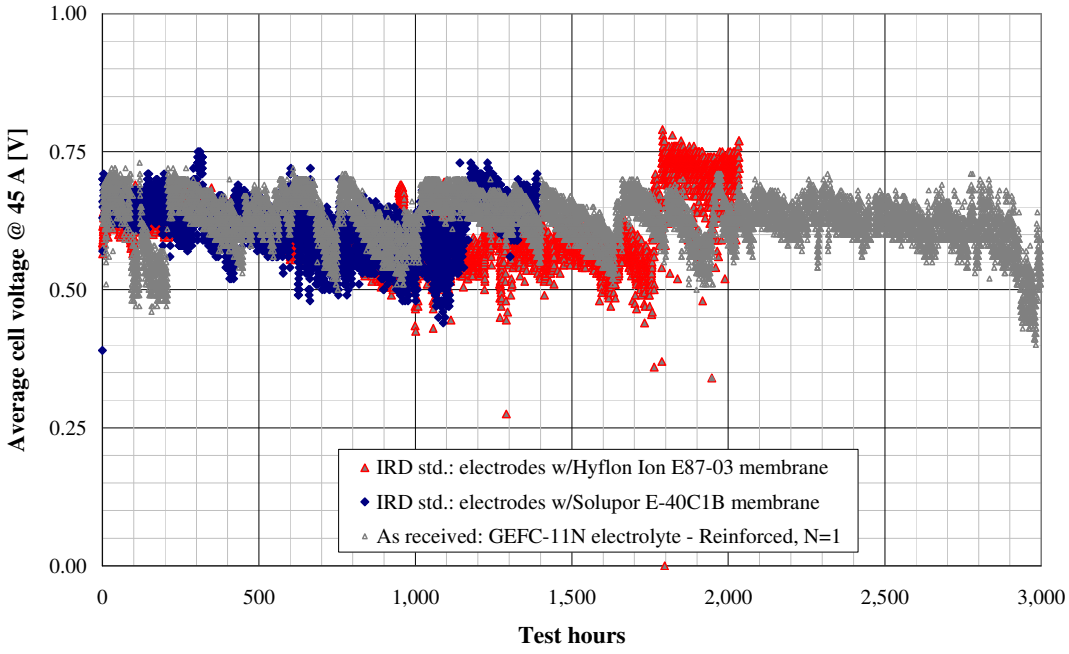


Figure 4.2.1 **Test result for the Hyflon Ion, GEFC and the Solupor membranes. Conditions for testing are indicated in table 4.2.1.**

4.3 Experimental membranes

As has been documented in section 2 membranes with conductivities relevant for fuel cell applications have been synthesised.
The membranes synthesised at DPC showed conductivities in the lower end of what is required and it was determined not to test these membranes in a fuel cell. The grafted membranes synthesised at IRD did show adequate conductivities and membrane electrode assemblies, MEA's, with several membranes were fabricated, see figure 4.3.1.

Figure 4.3.1 156 cm^2 MEA prepared with a grafted membrane.

Unfortunately the process of preparing a MEA involves conditions that are not favourable for the membrane, namely heat, pressure and hot, dry conditions. Under these circumstances the grafted membranes are very prone to crack resulting in gas cross over in the FC. Large MEA's tend to crack more easily than small MEA's.
Large, 156 cm^2 FC were put to FC test. However, these MEA did not perform well due to gas cross-over. Unfortunately no FC result have been acquired with small cells since the apparatus for testing the small cells have been under reconstruction.
The procedure for preparing MEA's with grafted membranes have to be revised, since the starting point for the preparation is a dry membrane. If the MEA can be prepared from a wet membrane and maintaining the MEA humid during the fabrication process there is a better chance to prepare the MEA without cracks. Thus the idea originally devised in a former project (PSO no.: 4073) will be re-initiated where hot, humid steam is used in a combination with pressure and heat see figure 4.3.2. The idea will be followed up in a project to come.

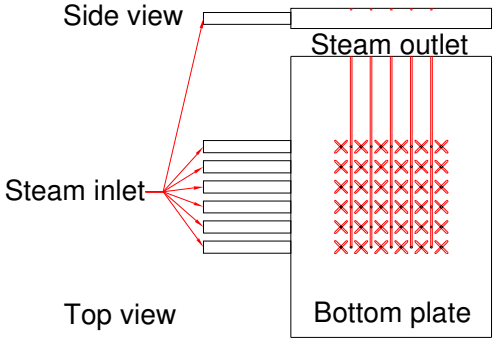


Figure 4.3.2 Bottom plate fixature and steam distributor for the MEA preparation device. Seen from side and top.

At the time of inauguration of this project IRD had also been testing a membrane M31 from Arkema. The M31 membrane, which is blended membrane of Kynar® PVdF and a proprietary polyelectrolyte, had a poor durability. However, Arkema has developed a new version, the M41 membrane, which is claimed to show similar stability compared to Nafion® [72], see figure 4.3.3 Unfortunately the membrane was not released for testing during this project. However the membrane will be tested in other projects.

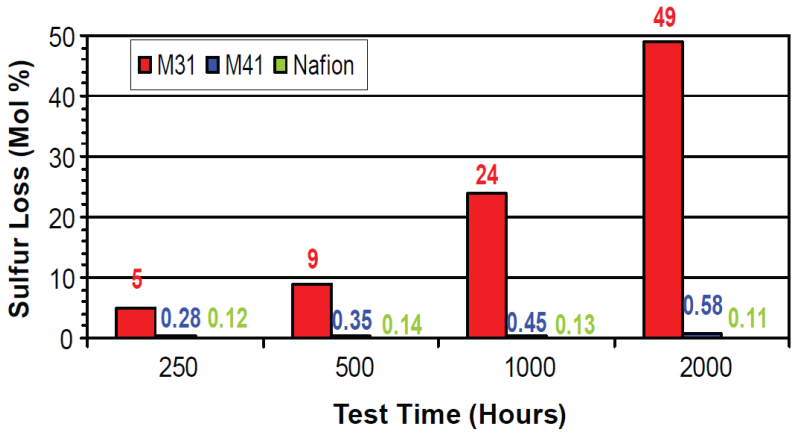


Figure 4.3.3 Ex-situ chemical stability of M31, M41 and Nafion® [72].

Abbreviations

1H NMR	Proton Nuclear Magnetic Resonance
Al	Aluminium
AMPS	2-Acrylamido-2-Methyl-N-PropaneSulfonic acid
AMS	□-MethylStyrene
ATRP	Atom Transfer Radical Polymerization
BAM3G	Ballard Advanced Membrane 3 Genereation
BoL	Beginning-of-Life
BoP	Balance-of-Plant
bpy	2,2'-bipyridine
CHP	Combined Heat and Power
DMF	DiMethylFormamide
DMF	N,N-DiMethylFormamide
DMSO	DiMethylSulfOxide
DOE	USA Department of Energy
DOG	Degree Of Grafting
DOS	Degree Of Sulfonation
DPC	Danish Polymer Centre
DVB	DiVinylBenzene
EDX	Energy Dispersive X-ray (often use in conjunction with SEM)
EoL	End-of-Life
ETFE	Ethylene-co-TetraFluoroEthylene
FC	Fuel Cell
FEP	Fluorinated Ethylene Propylene
GDL	Gas Diffusion Layer
HT	High Temperature
IEC	Ion Exchange Capacity
IRD	Innovation Research and Development (Company)
kGy	kilo Gray (measure of radiation dose)
LT	Low Temperature
MAN	MethAcryloNitrile
MEA	Membrane Electrode Assemblies
MTY	MethylsTYrene
NMR	Nuclear Magnetic Resonance (a prefix indicates type of NMR e.g. H1-NMR indicates proton NMR and F19-NMR indicates fluorine NMR on the F19-isotope).
OCV	Open Cell Voltage
PA	PolyAmide
PAMPS	Poly-2-Acrylamido-2-Methyl-N-PropaneSulfonic acid
PDI	PolyDispersity Indices
PE	PolyEthylene
PEM	Proton Exchangeable Membrane (or Polymer Electrolyte Membrane)
PET	PolyEthyleneTerephthalate
PFS	PentaFluoroStyrene
PHS	PolyHydroxyStyrene
PrS	1,3-PropaneSultone
PS	PolyStyrene
PSSA	PolyStyreneSulfonic Acid
PTFE	Polytetrafluoroethylene (Teflon)
PTFHS	Poly-2,3,5,6-TetraFluoro-4-HydroxyStyrene
PTFMS	Poly-2,3,5,6-TetraFluoro-4-MethoxyStyrene

PTFSS	Poly-2,3,5,6-TetraFluoro-4-SulfoStyrene
PVdF	PolyVinylideneFluoride
SDU	University of Southern Denmark (SydDansk Universitet)
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
SoA	State-of-the-Art
SS	StyreneSulfonate
TBY	para-Tert-ButylstYrene
TFHS	2,3,5,6-TetraFluoro-4-HydroxyStyrene
TFMS	2,3,5,6-TetraFluoro-4-MethoxyStyrene
TGA	ThermoGravimetric Analysis
UHMWPE	Ultra High Molecular Weight PolyEthylene,
UPS	Uninterrupted Power Supply
VS	VinylSulfonate

Published material

Controlled Synthesis of Fluorinated Block Copolymers with Pendant Sulfonates
Dimitrov, Ivaylo | Jankova, Katja | Hvilsted, Soren
Polymer Preprints. Vol. 48, no. 2. Aug. 2007

Synthetic Strategies for the Preparation of Fluorinated Polymers with Pendant Sulfonates
Dimitrov, Ivaylo; Jankova Atanasova, Katja; Hvilsted, Søren
Type: Conference contribution (posters, abstracts) - Conference abstract
Presented at: STIPOMAT Conferencee - 4, 2008, Lacanau, France

Controlled Synthesis of Fluorinated Copolymers with Pendant Sulfonates
Dimitrov, Ivaylo ; Jankova Atanasova, Katja ; Hvilsted, Søren
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(DOI: 10.1002/pola.23087) , vol: 46, issue: 23, pages: 7827-7834, 2008,
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Betydning af graden af tværbinding med divinylbenzen for sulfonerede polystyrene- og poly(methylstyrern-co-tert-butylstyren)podede ETFE-membraners egenskaber som polymerelektrytmaterialerr i methanolbrændselsceller
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